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NEW CONCEPTS OF THE SOLID STATE*

By Sir C. V. Raman

My first duty is to thank the authorities of the Nagpur University on behalf of the Indian Academy of Sciences for the invitation which has enabled the Annual Meeting of the Academy to be held this year under the auspices of the University. The Fellows of the Academy deeply appreciate the labours of the Chairman and members of the local Committee and of Prof. Moghe in making the arrangements for the meeting and are grateful for the hospitality which has been generously provided for the occasion.

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For good or for evil, we live in an age of science. No one who is familiar with the history of science would fail to recognize the great influence which has been exercised on its progress by the work of the various national academies of science, as for instance the Royal Society of London and the Academy of Sciences at Paris. The publications of these academies are the primary records of scientific discovery and invention in their respective countries. To no small extent, also, the Academies have been responsible for the promotion and encouragement of research work and for the co-ordination of the research activities of the Universities. During the seven years the Indian Academy of Sciences has been in existence, it has striven to fulfil these functions in our country. The *Proceedings* of the Academy which have appeared punctually, month after month, embody the best part of the research work done in most of the Indian Universities. It is greatly to be desired that these Universities appreciate what the Academy is doing for them and help the Academy to carry on under the present difficult conditions.

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I propose to devote my address this year to an exposition of the new ideas concerning the solid state of matter which have emerged from recent investigations made at Bangalore. The vast majority of actual solids are crystalline in structure and are either single crystals or else consist of polycrystalline aggregates. The gateway to an understanding of the solid

* Presidential Address to the Indian Academy of Sciences at the Annual Meeting held at the Nagpur University on the 24th of December 1941.

state is therefore to be found in the study of crystals. The most effective starting point for such a study is, again, the ultimate structure or atomic architecture of the solid. The physics of the solid state of matter indeed concerns itself largely with the relationship between the atomic grouping in space which characterizes a crystal and the physical behaviour of the solid in various circumstances.

As is well known, crystals often possess beautiful external forms with specific geometric features. The symmetry characters of these geometric forms stand in the closest relation to the physical properties of the solid, such relationship being most evident when we consider those properties which vary with direction. The study of the geometric forms and of the physical properties of crystals resulted in the classification of crystal forms into six or seven systems and their further sub-division into thirty-two classes of crystal symmetry. It is natural that crystallographers were led by such studies also to speculate on the features in the internal architecture of crystals to which could be ascribed the external symmetry properties manifested by them. The theoretical investigations which dealt with this problem resulted in the recognition that a crystal is essentially a repetitive pattern in space and that the material particles of the solid are arranged in regular geometric order in a three-dimensional space-lattice. The discovery of the 14 possible kinds of space-lattice and of the 230 possible ways of grouping the atoms, each in its own appropriate type of space-lattice and coming under one or another of the 32 possible symmetry classes, gave the necessary precision and completeness to such general notions of crystal architecture.

The ideas of the mathematical crystallographers of the nineteenth century found a spectacular confirmation in Laue's great discovery made in 1912 of the diffraction of X-rays by the space-lattice of crystals. During the thirty years which have elapsed since that discovery, a vast amount of detailed knowledge regarding the structure of individual crystals has been built up by the labours of the X-ray crystallographers. Around such knowledge, again, there has been a great deal of discussion regarding the nature of the forces which held together the atoms, ions or molecules in a crystal in the form of a coherent solid.

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It must be recognized that the concept of a regularly ordered assemblage of atoms, ions or molecules in a space-lattice is only a static description of crystal structure and does not suffice to give a complete view of the solid state. That the density and many other physical properties of

a solid vary with temperature is clear indication that the atomic positions in a crystal are subject to disturbance by thermal agitation. A description of the possible atomic movements in a crystal is thus as important for crystal physics as a knowledge of the static structure. In other words, a dynamic picture of the crystalline state is required as a complement to the static picture furnished by the space-group theory. The possible modes of atomic vibration would evidently be determined by the atomic groupings in the crystal lattice and the forces that come into play when such grouping is disturbed. It follows that the static and dynamic aspects of crystal architecture should stand in the closest relationship to each other.

A dynamic concept of the solid state is necessarily the starting point in any consideration of the thermal properties of a crystal, *e.g.*, its specific heat, thermal expansion or thermal conductivity. It is equally fundamental in any attempt to elucidate such physical properties of solids as are notably influenced by temperature, *e.g.*, the electrical resistivity of metals. The subject of crystal dynamics assumes a special importance in considering the effects arising from the propagation of electromagnetic waves through crystals, *e.g.*, the scattering of light or the diffraction of X-rays. Spectroscopic and X-ray studies on crystals indeed afford us a penetrating insight into the problems of the solid state.

* * * *

The theorists who have handled such problems in the past have proceeded by carrying over notions derived from the classical theory of vibrating elastic solids into the domain of atomic dynamics. The history of physics during the present century suggests that all such extrapolations from macroscopic to atomic concepts must be regarded with caution. The extrapolations made in the Debye and Born theories of crystal dynamics do not, however, appear to be justified even from a purely classical point of view. It is not surprising, therefore, that the conclusions derived from these theories fail to survive the test of comparison with the experimental facts in several different branches of research. Before we proceed to consider evidence of this kind, it appears desirable to examine the foundations on which these theories rest.

* * * *

We may, in the first instance, comment on the well-known specific heat theory of Debye which has had the run of the text-books of physics for many years and even yet seems to be in favour. The theory assumes that the thermal energy of a solid may be identified with the energy of elastic waves travelling within it, and gives an expression for the energy in terms

of the velocities of these waves. That these assumptions are unjustifiable is evident from Debye's own formulæ. For, the calculation shows that a very large proportion of the elastic vibrations must be assumed to possess wave-lengths comparable with the lattice spacings of the crystal. Their frequencies also become comparable with those of the vibrations of the individual atoms. Even according to the classical principles, vibrations of such short wave-lengths and high frequencies could scarcely be expected to travel through the crystal with the assumed acoustic velocities. Indeed, the familiar fact that thermal energy does not travel at all but only diffuses with extreme slowness in solids is a clear disproof of the basic assumptions of the Debye theory. Far from supporting the postulates of the theory, the facts point to exactly the opposite conclusion, namely that no sensible part of the thermal energy of solids consists of the elastic vibrations of macroscopic physics.

The so-called postulate of the "cyclic lattice" on which the crystal dynamics of Born is based was introduced by him as a mathematical device to escape the difficulties which he believed to arise from the unspecified conditions at the external boundary of the crystal. The postulate in effect prescribes "wave-lengths" for the atomic vibrations in the crystal which bear no relation to its internal architecture but are related to its external dimensions in exactly the same way as the elastic vibrations of macroscopic physics. The postulate of the cyclic lattice has no theoretical justification and its introduction makes Born's approach to the problem of crystal dynamics wholly unreal and no less open to criticism than the theory of Debye.

The fallacy of the basic ideas underlying the Debye and Born theories becomes evident when we consider the nature of the vibrations within a solid indicated by the classical theory of elasticity. The form and size of the external boundary of the solid determines the possible modes of elastic vibration. In each individual vibration, the motion at all points within the solid has a specifiable frequency and a coherent phase-relationship. But there would be an immense number of such modes with varying frequencies. The superposition of all such modes, assumed to be co-existent, would therefore result in the agitation within the solid being of a completely chaotic character, varying from point to point and from instant to instant without any recognizable periodicity in space or recurrence in time. Thus, in effect, the assumptions made in the Debye and Born theories are equivalent to the assertion that while the static arrangement of the atoms in a crystal is one of perfect order and regularity, the dynamic character of their movements is one of perfect chaos and disorder, indeed exactly of the same

kind as the movements or vibrations of the molecules of a gas. This conclusion is obviously so improbable that we may well feel justified in rejecting without hesitation the premises on which it is based.

* * * *

A crystal, as we have seen, is a periodic array of similar particles, similarly situated and capable of influencing each other's movements. It follows that the vibrations of such an assemblage should exhibit a high degree of orderliness, approaching the ideal of a perfectly co-ordinated vibration in which the frequency, amplitude and phase are identically the same throughout the crystal. To picture such a vibration, we may first consider the group of the atoms present in an individual cell of the space-lattice. The internal vibrations of such a group would comprise several distinct modes determined by the number of atoms present. Each such vibration may then be pictured as occurring in identically the same way in every cell of the crystal lattice. Geometrically, such an oscillation could be represented as a periodic movement, relative to each other, of the interpenetrating simple lattices of similarly placed atoms of which any crystal may be regarded as built up. Such a vibration would have a uniquely definable frequency, and the vibration spectrum of the crystal would therefore consist of a finite number of discrete monochromatic frequencies.

Thus, instead of an infinite array of choatic movements varying arbitrarily in phase from cell to cell of the crystal, and having a continuous spectrum of frequencies, we obtain a finite group of vibration modes with space-patterns coinciding with the lattice structure of the crystal and having a set of discrete monochromatic frequencies. These vibrations are essentially periodic changes in the fine structure of the crystal and do not involve mass movements of the substance of the solid. Hence, neither the existence of an external boundary nor the conditions restraining its movements can have any influence on such vibrations.

The most appropriate choice for the space unit of the three-dimensional repetition-pattern of the atomic vibrations is evidently that which enables all the modes possible to be included without redundancy. Hence the appropriate choice is not the cell having the smallest dimensions or including the least number of atoms, but one which is fully representative of the crystal structure and symmetry. In the majority of crystals, the number of atoms included in such a space-unit would be fairly large. Hence, the internal vibrations of the group of atoms contained in it would comprise the largest proportion of the available degrees of freedom of movement, indeed all except a small residue representing the translatory movements

of the chosen cell. To enable these latter to be included in the scheme, we may consider the internal vibrations of a group of atoms contained in the cells of a super-lattice having cells of twice the linear dimensions and therefore of eight-fold volume. Proceeding in this way by successive steps, the vibration spectrum of the crystal could be developed with all desirable completeness as a set of monochromatic frequencies.

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It will be realised that the geometric characters as well as the frequency distribution of the atomic movements in crystals obtained in this way would be radically different from those indicated by the Debye and Born theories. It is evident also that the new concepts involve striking differences in the spectroscopic, X-ray and thermal behaviour of crystals as compared with those derived from the older ideas. The issues arising between the new and the older concepts are thus capable of being brought to an exact experimental test.

* * * *

The atomic vibrations in crystal lattices are accessible to optical and spectroscopic investigation in several different ways. A method which makes the entire frequency range conveniently accessible to observation is the spectroscopic study of the scattered radiations emerging from a crystal traversed by monochromatic light. The most striking feature revealed by such studies with crystals is the extreme sharpness of the displaced lines appearing in their spectra. Even in those cases where the lines are somewhat diffuse, they sharpen into the finest lines when the crystal is cooled down to low temperatures. The monochromatism of the lattice frequencies thus indicated is especially significant when the vibrations are observable only in the crystalline state, in other words when the lines disappear in the molten or dissolved material. These facts are wholly inconsistent with the Debye and Born theories. Indeed, it may be said that the character of the spectra observed even with the simplest of crystals bears no resemblance to the diffuse continua suggested by these theories. Evidence confirmatory of the new concepts of crystal dynamics is also furnished by the absorption and luminescence spectra of crystals observed at low temperatures, *e.g.*, diamond. Here again, the lattice spectrum is revealed as a set of discrete monochromatic frequencies stretching down to low values, in startling contrast with the conclusions of the Debye and the Born theories.

* * * *

As already explained, the new concepts indicate a close correspondence between the static structure and the dynamic behaviour of a crystal,

in other words that the atomic vibration patterns are either identical with or closely related to the lattice structure of the crystal. As an immediate consequence of this relationship, it follows that the lattice planes of a crystal should give two distinct types of X-ray reflection—a dynamic reflection with altered frequency in addition to the static reflection of unmodified frequency discovered by Laue. The more perfectly co-ordinated is the oscillation of the lattice structure, the more perfect would be the geometric character of the dynamic X-ray reflections. Hence, these reflections should be shown in the most striking way by diamond-like structures in which the entire crystal is practically a single molecule and less perfectly by other crystals in which the lattice structure is of a more open kind.

That the lattice planes in crystals do give the new type of dynamic X-ray reflection here indicated and that such reflections are incapable of being explained on the older theories was discovered and announced by myself and Dr. Nilakantan in March 1940. In a symposium of fifteen papers published in the *Proceedings* of the Academy for October 1941, the theory of these new X-ray reflections, their relation to quantum mechanics and the experimental facts as observed with diamond and numerous other crystals have been thoroughly explored. It has been proved that the experimental facts are, on one hand, fatal to the Debye and Born theories and that on the other hand, they give the strongest support to the new concepts of the solid state.

* * * *

To the pioneer investigations of Einstein, we owe the basic principles of the quantum theory of the specific heat of solids. He showed clearly that the thermal energy of a crystal stands in the closest relation to its optical properties and could, in fact, be expressed in terms of the characteristic frequencies of atomic vibration appearing in the infra-red region of frequency. In his earliest paper, Einstein suggested that the atomic frequencies could be assumed to be monochromatic. Considering one such characteristic frequency in the case of diamond, he evaluated the same from the specific heat data. It will be seen from our present discussion that the basic assumption of monochromatism was justified, and that the only amendment needed in Einstein's theory was the inclusion of the full number of discrete monochromatic frequencies demanded by the lattice structure of the crystal with the appropriate statistical weights. It is also seen that the application of the macroscopic theory of elastic vibrations due to Debye, successful though it seemed at the time, was, in reality, a false step.

In a symposium of seven papers published in the *Proceedings* of the Academy for November 1941, the problem of the thermal energy of crystalline solids has been discussed fully from the new point of view and compared with the experimental data for a variety of substances. In several cases where the necessary spectroscopic data were available, these have been effectively made use of. In other cases, *e.g.*, metals, the specific data themselves have been utilised to evaluate the atomic frequencies. The most significant fact which emerges from the symposium is that the experimental facts in several cases which refused obstinately to fit into the Debye and Born theories find a natural explanation in the new concepts without the aid of any special hypothesis.

* * * *

Summary

The postulates on which the Debye theory of the specific heat of solids and the Born crystal dynamics are respectively based have been critically examined and shown to be theoretically untenable. Since a crystal is a three-dimensionally periodic grouping of similar oscillators coupled together, it follows that the modes of vibrations possible would be also space-periodic, the geometric modes being determined by the characters of the atomic space-grouping in the crystal. They would further form a finite and enumerable set of monochromatic frequencies. The spectroscopic, X-ray and thermal behaviours of a crystal would on these views be radically different from those consequent on the Debye and Born theories. The experimental facts are found to contradict the conclusions of these theories and on the other hand, to be in full accord with the new concepts.

STUDIES IN EDUCATIONAL STATISTICS:

Part IV. A Criterion of Examination Efficiency by the Method of Adjusted Plot Yields

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(Communicated by Dr. K. R. Ramanathan)

In 'Studies in Educational Statistics: III'[1] reference was made to Prof. D. D. Kosambi's suggestion to treat the numbers of students who appeared and passed in an examination as preliminary and experimental plot yields and then adjust the numbers of passes as in Ex. 46·1 of R. A. Fisher's *Statistical Methods for Research Workers*. The present note is the result of working out the suggestion. Its main aim is to suggest an exact criterion of efficiency for comparison of educational institutions.

According to the common way of thinking, when different colleges present different numbers of students for an examination, their examination efficiency is compared by their percentages of passes. Accepting this I had applied the method of analysis of variance to these percentages in former Studies and determined the ranking of Bombay colleges of long standing on the results of the I.A., I.Sc., B.A. and B.Sc. examinations. But looking closer it will be seen that the percentage of pases is a doubtful criterion of efficiency. For, suppose a college sends for an examination three candidates and all pass; another college sends 100 and only 90 pass. On the percentage basis the first college must be considered superior to the second. But no teacher and few students or others will admit that the first college is so decidedly superior to the second. From my own teaching experience as well as that of my colleagues I can say that a far greater effort is needed to get 100 or even 90 pass out of 100 than to get 3 pass out of 3; clearly the size of the sample must be allowed for in some way in any proper test of efficiency.

Kosambi's suggestion referred to above amounts to eliminating the effect of the variation in the numbers appearing for an examination from the result of the examination. While considering the results of the I.A., I.Sc., B.A. and B.Sc. examinations if x_1 is the number that appeared at I.A. (or I.Sc.) and x_2 that appeared at B.A. (or B.Sc.), each of the numbers passing these examinations (y_1 and y_2 respectively) may be adjusted by eliminating the effect of variation both in x_1 and x_2 or by eliminating the effect of only one of these, *i.e.*, x_1 from y_1 and x_2 from y_2. The analysis of variance and of covariance of the numbers so adjusted is given in Tables I and II. These tables will

TABLE

Numbers of Passes

(Analysis of Variance

		D.F.	S.S.	M.S.	F.	Reduced S.S.	Reduced M.S.	Ratio
I.A.	Colleges ..	12	23840·31	1986·69	8·83***	20899·29	1741·61	7·74***
	Years ..	19	32500·55	1710·55	7·60***	31771·42	1672·18	7·43***
	Residual ..	227	51066·28	224·96	s.d. = 14·99			
	Total ..	258	107407·14	416·31				
B.A.	Colleges ..	12	56343·70	4695·31	89·32***	35313·93	2942·83	55·98***
	Years ..	19	11157·11	587·22	11·17***	9802·26	515·91	9·81***
	Residual ..	227	11932·72	52·57	s.d. = 7·25			
	Total ..	258	79433·53	307·88				
I.Sc.	Colleges ..	7	677·76	96·82	$(1·02)^{-1}$	588·50	84·07	$(1·18)^{-1}$
	Years ..	19	14546·30	765·59	7·73***	13588·07	715·16	7·22***
	Residual ..	132	13070·60	99·02	s.d. = 9·95			
	Total ..	158	28294·66	179·08				
B.Sc.	Colleges ..	7	7321·82	1045·97	26·46***	5235·27	747·90	18·92***
	Years ..	19	3326·33	175·07	4·43***	1981·77	104·30	2·64**
	Residual ..	132	5217·28	39·52	s.d. = 6·29			
	Total ..	158	15865·43	100·41				

Notation and Formulæ used

x_1: No. appeared I.A. or I.Sc. $\Sigma y_1'^2 = \Sigma y_1^2 + a^2\Sigma x_1^2 - 2a\Sigma x_1 y_1$

x_2: „ „ B.A. or B.Sc. $\Sigma y_2'^2 = \Sigma y_2^2 + b^2\Sigma x_2^2 - 2b\Sigma x_2 y_2$

y_1: „ passed I.A. or I.Sc.

y_2: „ „ B.A. or B.Sc. $\Sigma y_1' y_2' = \Sigma y_1 y_2 + ab\Sigma x_1 x_2 - a\Sigma x_1 y_2 - b\Sigma x_2 y_1$

$a = \Sigma x_1 y_1 \div \Sigma x_1^2$; $b = \Sigma x_2 y_2 \div \Sigma x_2^2$

		a	$2a$	a^2
Values of Constants	I.A.	·4478	·8956	·2005
	B.A.			
	I.Sc.	·4379	·8758	·1918
	B.Sc.			

I

after Single Adjustment

and Co-Variance)

X^2	XY	Y^2	r	n'	S/n'	Ratio
23840·31	27166·63	56343·70	·74**	22	1118·24	22·11***
32500·55	9902·97	11157·11	·52*	36	451·80	8·93***
51066·28	9328·59	11932·72	·38***	452	50·56	
107407·14	46398·19	79433·53	·50	514	155·38	
677·76	1079·84	7321·82	·48	12	162·37	5·15***
14546·30	4169·81	3326·33	·60**	36	154·66	4·91***
13070·60	249·89	5217·28	·03	262	31·50	
28294·66	5499·54	15865·43	·26	314	65·16	

} For variance y' is the adjusted value of corresponding y.

For co-variance $n' = 2$ (D.F.$-$ 1). $S^2 = \Sigma x^2 \cdot \Sigma y^2 - (\Sigma xy)^2$.

N.B.—All variates are taken as measured from the mean

ab	b	$2b$	b^2
·3179			
	·7100	1·42	·5041
·2802			
	·6400	1·28	·4095

TABLE II

Numbers of Passes after Double Adjustment

(Analysis of Variance and Co-Variance)

		D.F.	S.S.	M.S.	F.	X^2	XY	Y^2
I.A.	Colleges ..	12	23839·56	1986·63	9·21***	23839·56	34471 60	61217·93
	Years ..	19	26620·36	1401·07	6·50***	26620·36	8223 26	10967·14
	Residual ..	226	48738·79	215·66	s.d. = 14·69	48738·79	9451·20	11894·56
	Total ..	257	99198·71	385·99		99198·71	52151·06	84079·63
B.A.	Colleges ..	12	61217·93	5101·49	96·93***			
	Years ..	19	10967·14	577·22	10·97***			
	Residual ..	226	11894·56	52·63	s.d. = 7·25			
	Total ..	257	84079·63	327·16				
I.Sc.	Colleges ..	7	765·53	109·36	1·14	765·53	1846·27	6817·76
	Years ..	19	11904·11	626·53	6·54***	11904·11	3492·14	3813·59
	Residual ..	131	12545·59	95·77	s.d. = 9·79	12545·59	141·08	5158·36
	Total ..	157	25215·23	160·61		25215·23	5479·49	15789·71
B.Sc.	Colleges ..	7	6817·76	973·96	24·73***			
	Years ..	19	3813·59	200·71	5·10***			
	Residual ..	131	5158·36	39·38	s.d. = 6·27			
	Total ..	157	15789·71	100·57				

Formulæ used:—x_1: No. appeared I.A. or I.Sc. $\Sigma x_1y_1 = a_1\Sigma(x_1^2) + b_1\Sigma(x_1x_2)$

x_2: „ „ B.A. or B.Sc. $\Sigma x_2y_1 = a_1\Sigma(x_1x_2) + b_1\Sigma(x_2^2)$ $y_1' = y_1 - a_1(x_1 - \bar{x}_1) - b_1(x_2 - \bar{x}_2)$

y_1: „ passed I.A. or I.Sc. $\Sigma x_1y_2 = a_2\Sigma(x_1^2) + b_2\Sigma(x_1x_2)$ $y_2' = y_2 - a_2(x_1 - \bar{x}_1) - b_2(x_2 - \bar{x}_2)$

y_2: „ „ B.A. or B.Sc. $\Sigma x_2y_2 = a_2\Sigma(x_1x_2) + b_2\Sigma(x_2^2)$ y' is the adjusted value of corresponding y.

For variance:—$\Sigma(y' - \bar{y})^2 = \Sigma y^2 + a^2\Sigma x_1^2 + b^2\Sigma x_2^2 + 2ab\Sigma x_1x_2 - 2a\Sigma x_1y - 2b\Sigma x_2y$

Suffix 1 or 2 being used for a, b, y as it is used for one or the other set

For co-variance:—$\Sigma(y_1' - \bar{y}_1)(y_2' - \bar{y}_2) = \Sigma y_1y_2 + a_1a_2\Sigma x_1^2 + b_1b_2\Sigma x_2^2 + (a_1b_2 + a_2b_1)\Sigma x_1x_2 - a_1\Sigma x_1y_2 - b_1\Sigma x_2y_2 - a_2\Sigma x_1y_1 - b_2\Sigma x_2y_1$

		a_1	b_1	a_2	b_2	a_1a_2	b_1b_2	$a_1b_2 + a_2b_1$
Values of Constants	I.A.; B.A.	·4168	·1486	·0096	·7021	·0040	·1043	·2941
	I.Sc.; B.Sc.	·3965	·1587	−·0225	·6728	−·0089	·1068	·2632

N.B.—All variates are taken as measured from the mean.

show that the *s.d.* in the analysis worked in both ways is almost exactly the same for all examinations. The analysis of variance by ' double adjustment ' is open to two objections. First the labour involved is disproportionately great for the advantage obtained. Secondly there appears no good reason why the number appeared at the Baccalaureate should be allowed for in testing the efficiency of the number passed at the Intermediate that precedes. The numbers appearing at the B.A. (or B.Sc.) are after all the result and not the cause of those that pass the I.A. (or I.Sc.). It may, however, be argued that the number passing at the B.A. must be affected by the number appearing at the I.A. two years earlier. But this effect is actually negligible as may be seen from the small numerical values of the corresponding regression coefficients. This is explained by the fact that a large number change colleges between the two examinations and the effect of the lower examination is further diluted by the number of students who leave college altogether and by those who reappear after failing at least once in the higher examination. For these reasons further details are worked only for the analysis after a ' single adjustment'. The notation and formulæ used as well as the values of the constants involved are given at the foot of each table.

The original purpose of this note was to find the ranking of colleges by the method of adjusted plot yields and to compare this ranking with that obtained by the percentage method of my previous *Studies*. This ranking by both these methods is given in table III. But I think that a far more important fact has emerged during the course of the investigation. I have remarked before in *Studies* II that the difference between years and between colleges may roughly be called the difference between nature and nurture; though the former includes the effect of varying examiners and the latter that of selection of students by colleges and *vice versa*. This difference is tested for any examination by comparing the two mean squares by the z test. In the case of the I.A. this difference in variation is insignificant. But in the case of the I.Sc. the difference in years is actually and significantly greater; I think this may be due to the vagaries of the examiners rather than to any intrinsic natural annual variation in the capacities of the students. Referring to the B.A. and B.Sc. it will be seen that the colleges in each case show significantly greater variation than the years. This shows that for the degree examinations the effect of college training and the difference between colleges is unmistakable. Two explanations may be offered for this; one, that both colleges and students show greater seriousness in preparing for these examinations; another, that the students, after the Inter, have to specialise in some particular field of study of their choice and therefore tend

TABLE

Ranking

	Intermediate Arts				Bachelor of Arts			
	By adjusted means		By percentage means		By adjusted means		By percentage means	
	College	Mean	College	Mean	College	Mean	College	Mean
1	St.X.	85·48	E.	70·8	St.X.	69·24	E.	81·4
2	W.	83·29	W.	63·3	E.	66·98	G.	79·4
3	E.	81·64	G.	59·6	W.	66·37	S.	79·1
4	G.	78·35	St.X.	58·4	G.	64·62	D.J.	78·8
5	S.	75·98	Bah.	58·1	D.J.	64·48	St.X.	77·8
6	S.P.	74·86	S.	58·1	S.	63·20	W.	77·5
7	F.	74·55	S.P.	55·9	S.P.	60·17	Bah.	72·9
8	Bah.	74·13	F.	55·4	Bah.	59·91	F.	70·9
9	D.J.	70·77	D.J.	53·9	F.	59·30	S.P.	70·4
10	Bar.	70·11	Bar.	52·1	K.	58·91	K.	69·3
11	K.	68·58	K.	51·0	R.	57·75	Bar.	67·5
12	R.	64·81	R.	45·1	Bar.	55·77	R.	67·5
13	Ex.	46·33	Ex.	43·2	Ex.	6·38	Ex.	44·2
c.d.	..	9·49	..	4·92	..	4·58	..	4·94

E.–Elphinstone; W.–Wilson; St.X.–St. Xavier's; G.–Gujrat; R.–Rajaram; Bar.–Baroda; K.–Karnatak; Ex.–Ex-students.

to select the college which has the best examination reputation in that subject. While such an explanation can be supplied from a teacher's experience, the phenomenon itself could not possibly have been noticed but for an accurate statistical analysis; as may be seen from the fact that this difference was not so marked in the analysis by the percentage method.

The correlation coefficient, *r*, between Intermediate and Baccalaurate passes for corresponding years shows, for the arts examinations, values which are significant and satisfactory though the value of the residual correlation is rather high. On the science side the

III

of Colleges

Intermediate Science				Bachelor of Science			
By adjusted means		By percentage means		By adjusted means		By percentage means	
College	Mean	College	Mean	College	Mean	College	Mean
G.	58·28	E.	63·8	E.	38·93	E.	79·5
St.X.	57·77	G.	59·7	St.X.	38·40	G.	78·6
E.	57·16	W.	53·3	Bar.	35·86	St.X.	75·3
W.	56·95	St.X.	52·6	G.	34·37	Bar.	74·3
Bar.	56·13	Bar.	51·6	W.	33·69	W.	73·7
D.J.	53·88	Ex.	49·8	D.J.	32·78	D.J.	66·2
F.	52·78	D.J.	49·2	F.	28·58	F.	58·9
Ex.	52·29	F.	48·0	Ex.	17·23	Ex.	43·9
..	6·29	..	5·32	..	3·98	..	6·86

F.–Fergusson; S.–Samaldas; D. J.–D. J. Sind Karachi; Bah.–Bahauddin; S.P.–Sir Parasurambhau.

only significant value of r is that for years. From the same table it is seen that taking the two arts examinations as a whole the effects of colleges and years are both highly significant by Kosambi's test[2]; and the same remark applies to the two science examinations. But the difference between colleges and years is significant at one per cent. level for the arts examinations, while it is not at all significant for the science examinations. This shows that for the science examinations the colleges are not discharging their duties as satisfactorily as for the arts examinations. Of course a slight allowance might have to be made for the fact that the number of colleges, considered for

the science examinations, is smaller than that considered for the arts examinations.

From Table III 'Ranking of Colleges' it may be seen that the only 'college' holding its rank (the last) in all examinations by both the criteria of efficiency is the ex-students group. Among other colleges the method of adjusted plot yields causes slight displacements one way or the other the most important being that of the Elphinstone College. By the percentage method, the Elphinstone College ranks first in all examinations. But by adjusted means the St. Xavier's College ranks first in the arts examinations and the Gujrat College ranks first in the I.Sc., the Elphinstone College (including Royal Institute of Science, Bombay) holding its own in the B.Sc. Among colleges in the Bombay Presidency, the St. Xavier's has the largest number of students; and the fact that in spite of its large numbers it ranks very high by either criterion and actually is first in the two arts examinations by adjusted means is a performance for which the management may well feel proud. But as a matter of fact, the large number itself of students in the college is most probably due to the reputation in examination efficiency which the college possesses in the student world; the intuitive and the exact criteria give coincident results. That the Elphinstone College is dislodged from its first rank by the percentages method indicates that it is necessary for a good criterion of efficiency to eliminate the effect of varying numbers. It may also be remarked that the Bombay colleges lead in almost all examinations. This may be ascribed primarily to the fact that the medium of instruction and examination in the Bombay University is English; and the standard of English in the metropolis is naturally higher than in the rest of the Presidency.

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FLUORESCENCE REACTIONS WITH BORIC ACID AND O-HYDROXY-CARBONYL COMPOUNDS, AND THEIR APPLICATION IN ANALYTICAL CHEMISTRY

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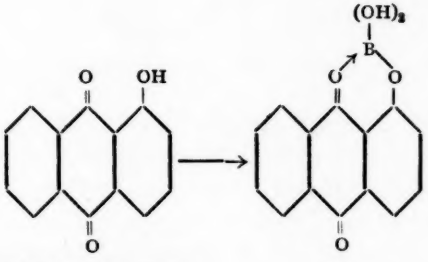
Fluorescence reactions for the detection of inorganic anions and cations are very few in number, and among these may be mentioned two examples involving boric acid. Of these two, the most important was proposed by Szebellédy and Gáal[1] for the detection of boric acid. This reaction depends on the fact that in a suitably buffered solution and in the absence of carbonates, heavy metals, etc., which interfere, boric acid yields with tincture cochineal an orange-yellow fluorescence visible under the ultra-violet light. The second example, mentioned by Meyer,[2] is that of the yellow fluorescence visible in daylight yielded by quinizarin (1 : 4-dihydroxy-anthraquinone) dissolved in concentrated sulphuric acid.

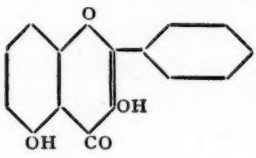
Feigl[3] observed that boric acid reacts with many hydroxy-anthraquinones yielding characteristic colour changes which can be used for either the detection of boric acid or the hydroxy-anthraquinones.[4] From a study of these reactions, he came to the conclusion that the colour changes are apparently due to the formation of inner complex (chelate) boric acid esters of the type shown below,

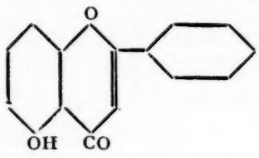


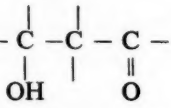
or similar boric-sulphuric acid esters.

In the course of the work which is in progress on the detection of boric acid in qualitative analysis, it was considered desirable to investigate the

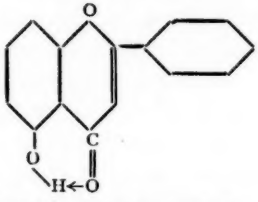
reaction with boric acid of the 5-hydroxy-flavonols and -flavones which also



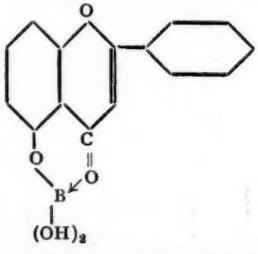


contain an identical reactive grouping  . It is well known

that in these compounds the 5-hydroxyl group exhibits a peculiarity in that it is difficult to methylate, and this is attributed to the fact that chelation exists between the hydrogen of the hydroxyl and the carbonyl oxygen as shown below. It, therefore, appeared quite probable that boric acid will



yield chelate compounds of the type shown below involving these two groups as in the case of the hydroxy-anthraquinones. Further, scattered through the literature are several examples of hydroxy-flavones and -flavonols which yield fluorescence visible in daylight when dissolved in sulphuric acid. Com-



parison of the constitutions of these compounds in relation to the fluorescence exhibited by them indicated that the 5-hydroxyl group generally exerted a batho-floric effect. From this again it appeared probable that chelation of the above kind would lead to interesting fluorescence changes which might serve for the detection of boric acid. A preliminary investigation showed that this was the case. Since the 5-hydroxyl group reacts as an ortho-group

to the carbonyl, the investigation was extended to the simple ortho-hydroxy-carbonyl compounds such as the ortho-hydroxy-acids, -aldehydes, and ketones with or without other substituents in the molecule, with a view to find out whether a satisfactory reagent for boric acid could be found among them. To throw light on the reaction, a few flavylium salts, polyhydric phenols and hydroxy-carbonyl compounds containing the hydroxyl in positions other than ortho to the carbonyl were examined. In all over forty compounds were examined.

Experimental

Solutions—

1. *Boric Acid.*—A solution of boric aicd in concentrated sulphuric acid containing 20 mg. of the former acid per c.c. was used.

2. *Reagent Solution.*—About 10–15 mg. of the substance under investigation was dissolved in concentrated sulphuric acid (5 c.c.) either in the cold or by slight warming. In case the solution was strongly coloured it was diluted with more acid. The solution was divided into approximately equal parts in each case and one of them used as blank.

Procedure—

The two halves of the reagent solution were placed in quartz test-tubes of approximately the same dimensions and to one was added 1 c.c. of boric acid solution. After mixing in the cold, the two solutions were examined for any fluorescence first in daylight and then under the Cenco Black Light Source.[5]

Results—

The colour of the fluorescence obtained is recorded in Table I.

Of all the compounds examined resacetophenone yields the best results with boric acid. It gives no fluorescence even under the lamp, when dissolved in sulphuric acid, but in the presence of boric acid in the cold it yields a bright blue fluorescence visible under the lamp. A preliminary examination of the applicability of this reaction for the detection of boric acid gave the following results:—

(*a*) Limit of Identification = 100 γ.

(*b*) Limit of Sensitiveness = 1 : 10,000.

It also appears probable that with a better source of ultra-violet light the sensitiveness can be considerably increased.

TABLE I

Reagent	Without Boric Acid		With Boric Acid		Remarks
	Day-light	Under lamp	Day-light	Under lamp	
Falvones and Flavonols					
1 Kæmpferol	Blue	Greenish yellow	Blue	Bright greenish yellow	Yellow solution, deeper yellow with boric acid,
2 Quercetin	Green	Greenish yellow	Deep green	Intense greenish yellow	Yellow colour deepened with boric acid. The green fluorescence of quercetin in conc. H_2SO_4 has not been observed before. Working with quartz test-tubes, however, this fluorescence is observed.
3 Morin	Bright green	Bright green	Bright yellowish green	Intense yellowish green	Addition of boric acid caused a deepening in the yellow colour of the solution.
4 Quercetagetin	Nil	Pale green	Nil	Pale green	Deep yellow solution. Difference is not prominent.
5 Gossypetin	Nil	Nil	Nil	Nil	Solution deep orange yellow.
6 3 : 7-Dihydroxyflavone ..	Light blue	Bright blue	Bright blue	Intense blue	Pale yellow solution. This result is surprising in view of the fact that the molecule does not contain a 5-hydroxyl.
7 7-Hydroxy-flavone ..	Blue	Intense blue	Blue	Intense blue	Almost colourless solution. No difference has been observed in the test from the blank.
8 Herbacetin	Nil	Greenish yellow	Nil	Greenish yellow	Orange solution. Difference is not marked.
9 Cannabiscetin	Nil	Yellow	Nil	Deep yellow	Yellow solution.
Flavanones					
1 Naringenin	Pale green	Greenish yellow	Deep green	Deep greenish yellow	Pale yellow solution; deeper yellow with boric acid.
2 Butin	Nil	Nil	Nil	Nil	Yellow solution; deeper yellow on adding boric acid.

	O-Hydroxy-ketones					
1	Resacetophenone ..	Nil	Nil	Nil	Bright blue	The solution is colourless and the fluorescence with boric acid is very prominent.
2	2 : 6-Dihydroxy-aceto-phenone	Nil	Nil	Nil	Yellowish green	Yellow solution. The fluorescence obtained is not so very prominent as with resacetophenone.
3	*w*-Methoxy-resacetophenone	Nil	Nil	Nil	Light green	Very pale yellow solution.
4	Phloracetophenone ..	Nil	Nil	Nil	Green	Yellow solution; fluorescence not so intense as with resacetophenone.
5	2-Methoxy-3 : 6-dihydroxy acetophenone	Nil	Nil	Nil	Pale yellow	Yellow solution; deeper yellow on adding boric aicd.
6	2 : 4-Dihydroxy-3-methyl acetophenone	Nil	Nil	Nil	Nil	
7	*w* : *p*-Dihydroxy acetophenone	Nil	Nil	Nil	Nil	
	O-Hydroxy-aldehydes					
1	Salicyl aldehyde	Nil	Nil	Nil	Greenish yellow	Deep orange solution.
2	β-Resorcylic aldehyde ..	Nil	Nil	Nil	Green	Brownish yellow solution.
3	γ-Resorcylic aldehyde ..	Nil	Nil	Nil	Nil	Deep orange solution.
4	4-Methoxy-2-hydroxy-benzaldehyde	Nil	Nil	Nil	Greenish yellow	Pale yellow solution.
5	7-Hydroxy-coumarin-8-aldehyde	Nil	Nil	Nil	Nil	
6	7-Hydroxy-3-methoxy-flavone-8-aldehyde	Nil	Nil	Nil	Nil	
7	5-Bromo-salicylaldehyde ..	Nil	Nil	Nil	Nil	
8	2-Benzoyl-phloroglucin-aldehyde	Nil	Nil	Nil	Greenish yellow	Yellow solution.
	O-Hydroxy-Carboxylic Acids					
1	Salicylic acid	Nil	Violet	Nil	Intense violet	Colourless solution.
2	Sulpho-salicylic acid ..	Nil	Violet	Violet	Intense violet	Colourless solution; fluorescence obtained is more intense than with salicylic acid.

TABLE I—(*Contd.*)

	Reagent	Without Boric Acid		With Boric Acid		Remarks
		Day-light	Under lamp	Day-light	Under lamp	
3	Nitro-sulpho-salicylic acid	Nil	Nil	Nil	Nil	
4	Nitrosalicylic acid ..	Nil	Nil	Nil	Nil	
5	β-Resorcylic acid ..	Nil	Nil	Nil	Bright violet	Colourless solution.
6	3-Methyl-4-methoxy-2-hydroxy-benzoic acid	Nil	Nil	Nil	Nil	
7	4-Methoxy-2-hydroxy-benzoic acid	Nil	Nil	Nil	Violet	Colourless solution; fluorescence not so intense as with β-resorcylic acid.
8	Orsellinic acid	Nil	Nil	Very pale violet	Deep violet	Colourless solution; fluorescence deeper than with β-resorcylic acid.
9	Ethyl orsellinate ..	Nil	Nil	Very pale violet	Deep violet	Pale yellow solution.
10	Dimethyl ether of orsellinic acid	Nil	Nil	Nil	Nil	
	Polyhydric Phenols					
1	Catechol	Nil	Nil	Nil	Nil	
2	Resorcinol	Nil	Nil	Nil	Nil	
3	Hydroquinone	Pale blue	Blue	Pale blue	Blue	No difference.
4	Pyrogallol	Nil	Nil	Nil	Nil	
	Flavylium Salts					
1	7-Methoxy-3 : 4′-di-hydroxy flavylium chloride	Bright green	Yellow	Bright green	Yellow	Yellow solution. No difference.
2	7-Methoxy-3 : 3′ : 4′-tri-hydroxy flavylium chloride	Green	Yellow	Green	Yellow	Brown solution. No difference.
3	7-Methoxy-3 : 3′ : 4′ : 5′-tetrahydroxy flavylium chloride	Very pale green	Yellow	Very pale green	Yellow	Deep brown solution. No difference.

Discussion

In agreement with the observations of Rangaswami and Seshadri,[6] in the group of flavones and flavonols examined, it is found that an increase in the number of hydroxyl groups as in the case of quercetagetin and gossypetin is unfavourable for the appearance of fluorescence with or without boric acid. The existence of a group of three hydroxyls in 5:6:7 and 5:7:8 positions has a considerable damping effect on the fluorescence. These results are similar to those obtained with aluminium recorded in a previous paper.[5] In the absence of the 5-hydroxyl, with the exception of 3:7-dihydroxy-flavone, no fluorescence change was observed either in the intensity or the colour. The flavanones also gave results consistent with the above conclusions. Besides these fluorescence effects it was observed that the addition of boric acid led to a deepening in the yellow colour of the sulphuric acid solution of these compounds.

In the case of the simple O-hydroxy-carbonyl compounds, while the results obtained were similar, it is remarkable that with the exception of salicylic and sulpho-salicylic acids, in the absence of boric acid none of them showed any fluorescence either in daylight or under the lamp; with boric acid, however, fluorescence was observed only under the lamp. In several cases it has been noticed that heating the solution of the substance in concentrated sulphuric acid with boric acid produced either an increase in intensity or a change in the colour of the fluorescence obtained in the cold. This may probably be due to the molecule undergoing sulphonation. This inference is supported by the observation that sulpho-salicylic acid in cold concentrated sulphuric acid yields under the lamp a violet fluorescence which is considerably more intense than that obtained with salicylic acid under almost identical conditions; an intensification of the fluorescence under the lamp was also observed with salicylic acid on heating with concentrated sulphuric acid. On the introduction of a nitro-group into the molecule of salicylic acid as well as sulphosalicylic acid, the fluorescence disappears completely thereby indicating that the nitro-group is considerably bathofloric in character.

In the group of O-hydroxy-carbonyl compounds examined, a few cases are exceptional in that they do not give any fluorescence effects with or without boric acid either in daylight or under the lamp. A common constitutional feature of these compounds is the existence of a substituent group between two hydroxyls one of which may be in the form of an ether or ester linkage as in the cases of γ- and α-benzopyrones. It appears, therefore, that the absence of fluorescence effects with boric acid need not necessarily indicate the absence of hydroxyl ortho to the carbonyl group.

Examination of the flavylium salts, polyhydric phenols and *p*-hydroxy-carbonyl compounds showed that in the absence of a hydroxyl ortho to the carbonyl, no fluorescence effects with boric acid are obtained.

Conclusion

(1) Addition of boric acid to O-hydroxy-carbonyl compounds dissolved in concentrated sulphuric acid, except in a few cases, brings about either a marked intensification or a change in colour of the fluorescence exhibited by them in daylight or under the lamp. In a few other cases fluorescence appears for the first time on the addition of boric acid. Since even the simpler O-hydroxy-carbonyl compounds yield these results with boric acid, it appears reasonable to conclude that this reaction will serve as a suitable method for the detection of O-hydroxy-carbonyl group. It must, however, be borne in mind that while the appearance of fluorescence, its intensification or a change in colour indicates the presence of a hydroxyl group ortho to the carbonyl, the non-appearance of the fluorescence effects described does not indicate the absence of this group.

(2) No fluorescence changes are observed with boric acid if the molecule of the compound under investigation does not contain a ketonic group ortho to the hydroxyl, so also in the absence of either of them or when they are present in positions other than ortho to each other.

(3) Sulphonation of the simpler O-hydroxy-carbonyl compounds brings about a marked change in the colour and intensity of the fluorescence; the sulphonic acid group appears to be markedly auxo-floric in character. It is remarkable that nitration or bromination, on the other hand, damps the fluorescence considerably.

(4) From the brilliant fluorescence effects given by resacetophenone, it is expected to develop into a useful reagent for the detection of boric acid on a semi-micro scale.

Further work along these lines is in progress.

The authors wish to express their thanks to Prof. T. R. Seshadri for the valuable help rendered in the course of this investigation.

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THE TIME DISTRIBUTION OF COSMIC RAYS

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1. Introduction

The problem of the probability distribution of α-particles emitted during radioactive decay has for long attracted the attention of workers in the field of nuclear physics. An experimental verification of the distribution law to be expected from complete time-randomness had an importance not only for the light it would throw on the basic decay mechanism at work, but also for introducing suitable correction for the finite resolving time of counting devices of nuclear particles. Most of the early experiments were done on the α-particles from polonium; the technique consisted in observing the particles by the scintillations produced on a suitable screen, and recording the instants of observation on a chronograph tape. The results were then analysed by either one of two methods. In that due to Bateman,[1] the fluctuations of the number 'n' of particles observed in small equal intervals of time were determined; whereas in that due to Marsden and Barratt,[2] the probabilities for the occurrence between successive arrivals of time intervals of duration greater than any particular 't' were calculated.

The earliest investigations made by Rutherford and Geiger,[3] by Marsden and Barratt,[2] and by Curie[4] all went to show that the α-particles from polonium obeyed the probability law to be expected from a complete time-randomness of the disintegrations. However, certain experiments of Kutzner[5] and later of Pokrowski[6] seemed to indicate that the concentration of the source investigated might have some effect on the statistics of the measured counts. These effects were later found to have no significance as far as the fundamental process of decay was concerned. Indeed Feather[7] who repeated some of the experiments of these two workers found " no evidence to show that the Marsden-Barratt distribution formula was not completely valid under the conditions obtaining ".

While therefore the position with respect to ordinary nuclear phenomenon seems now to be firmly established, a direct experimental test of the time distribution of cosmic rays does not appear to have been made. It

has of course been assumed, perhaps reasonably, that the arrivals of cosmic rays follow a perfectly random law; and indeed all counter experiments on cosmic rays have been corrected for the finite resolving time of the apparatus by using this assumption. But the fact that most of the cosmic ray particles at low levels are secondaries, and that often two or more particles from the same primary are present and capable of detection by the recording apparatus, makes it at least conceivable that the complete time-randomness of the arrivals of the particles may be disturbed. With this in view the present experiment was undertaken; and the question whether or not it was possible with the arrangement used to detect such an effect will be discussed in detail at a later stage.

2. *Theory of Random Fluctuations*

A very general treatment of the subject has been given by Ruark and Devol[8]; and several other authors have considered the various aspects of the problem. It can easily be shown that for perfectly random arrivals, the chance that 'n' particles arrive in a time 't' is given by the well-known formula of Bateman, *viz.*,

$$w_n(0, t) = \frac{x^n}{n!} e^{-x} \qquad (1)$$

where '$x = ft$' is the mean number of particles that arrive in the interval t. fdt, the probability that one particle would arrive in time dt, is naturally independent of 't' in the case considered. When we have a distribution of this kind, the standard deviation is $x^{\frac{1}{2}}$; and therefore the Lexian ratio Q^2, or the ratio of the (standard deviation)^2 and the mean is unity. The value of Q^2 gives us a quantitative measure of how far any given distribution agrees with the Bateman law. The dispersion is called supernormal or subnormal according to whether Q^2 is greater or less than unity. A subnormal dispersion indicates that we have in the distribution a larger number of small intervals than would be expected from the normal law. The value of making a Bateman analysis, *i.e.* to study how the number of particles in any given small time interval fluctuates about the mean number expected, is that we thereby get a quantitative measure of the goodness of fit between experimental results and the theory.

For the Marsden-Barratt analysis we have to know the theoretical probability for the occurrence between successive particles of time intervals of duration greater than any t. This can easily be derived from the Bateman formula (1) by considering the case where $n = 0$. The required probability is then:

$$\rho_t = e^{-ft}. \qquad (2)$$

We have here only made the arbitrary instant, at which we start the Bateman interval, coincide with the occurrence of each successive arrival. Thereby no fallacy is introduced into the argument as the probability $f(dt)$ is independent of time. If N_0 be the total number of intervals between the random arrivals, then the number of intervals N_s of duration greater than t_s is given by

$$N_s = N_0 \, e^{-\frac{t_s}{\overline{T}}}, \tag{3}$$

where $\overline{T}$ is the mean time interval and is equal to $1/f$. By taking logarithms we therefore get the linear relation

$$\log N_s = \log N_0 - \frac{t_s}{\overline{T}} \log e. \tag{4}$$

This is of a very suitable form for comparison with experimental data, because all the measured values of $\log N_s$ when plotted against t_s should fall on a straight line.

3. *Experimental*

In the present series of experiments, cosmic rays were detected by means of Geiger-Müller counters. All the counters used were of the Trōst fast self-quenching type; and the treatment of the counter copper cylinders was done according to the method described by Neher.[9] The counters were filled with a mixture of argon and petrol-ether; and when operated at a potential of about 1200 volts, they possessed plateaux of 150–200 volts. The efficiency of the counters, as experimentally found from a comparison of double and triple coincidences according to the usual method, came to greater than 95%.

Recently Driscoll *et al.*[10] have studied Geiger counter statistics by means of a completely electrical arrangement for discriminating between time intervals of varying durations. On using γ-rays from a sealed radium source to operate their counter tubes, they found that argon filled counters gave a time distribution of pulses in excellent agreement with fluctuation theory; a hydrogen filled counter however showed marked deviation. The use of argon filled counters in the present case was therefore expected to bring out faithfully the true statistics of cosmic ray arrivals. For, though Driscoll has not used alcohol vapour counters, the presence of the vapour should have no effect on the experiment so long as spurious discharges are not present to any appreciable extent. The existence of a fairly good plateaux in the counters used goes to show that this mechanism can be neglected.

The high voltage for the counter was obtained from an electronic voltage regulator[11] fed by a 2000 volt transformer. The central wire of the Geiger-Müller tube was directly connected to the grid of the first amplifier valve

and the subsequent connections are shown in Fig. 1. For the purpose of discriminating between time intervals of different duration it would have been possible to use the electrical method given by Driscoll, or the more elegant apparatus of Roberts[12] who has studied the statistical operation of various Geiger counter quenching circuits. But in the present case it was thought desirable to employ the more direct method of registering the arrivals of cosmic rays on a chronograph tape and then make both a Marsden-Barratt and a Bateman analysis of the record. Such a procedure, though laborious has obvious advantages; specially as it can with quite good accuracy reach the same order of small time intervals as the interval meter developed by Driscoll. The record from electrical time interval meters does not lend itself to a Bateman analysis and hence a quantitative criterion of goodness of fit, namely the value of Q^2 cannot be found. Besides, in experiments with cosmic rays we usually deal with much lower counting rates than in the case of nuclear disintegration phenomenon; and consequently the number of counts missed due to the finite resolving time of the recorder is also small.

The pulse from the Geiger counter was so fast that it was necessary to lengthen it before it could operate the chronograph pen. It was first tried to work the pen from the output current of a multivibrator circuit operating a telephone call counter (see Fig. 1 B). A resolving time of 1/15 second was attained in this way but there were two objections for using this method. It was thought that a multivibrator circuit, though operating normally for regular pulses, might have a tendency under certain circumstances to count double. This was in fact observed; and in some experiments done with this method, a larger number of small intervals was obtained than what we should expect from a random law. The second objection to this was that the call counter formed the limit for the resolving power, while the pen by itself was capable of registering much quicker pulses. Hence the method that was finally adopted consisted in a lengthening of the Geiger counter pulse by the use of high resistances and capacitances in the amplifier. This explains the unconventional values of some of the components shown in Fig. 1 A. The moving coil operating the pen of the chronograph was connected in series with the plate resistor r_6 of the second stage 57 tube; and the size of the deflection of the pen could be controlled by changing the cut-off bias voltage V_1 on this tube. A value of 10 volts for the bias was found to be suitable for most of the experiments undertaken. The object of the plate resistor r_6 was to generate a sufficient voltage pulse to operate the multivibrator counting unit shown in Fig. 1 B. The simultaneous running of this unit along with the chronograph pen was found to be very helpful in order to know the progress of the experiment. From the total counts registered

by the call counter, it was immediately possible to have an idea of the satisfactory operation of the apparatus during a run. The Fig. 1 A shows the arrangement as used for measuring double coincidences between Geiger counters; but when a single Geiger counter was under investigation it was only necessary to remove one of the two Rossi tubes from its socket and use the other singly.

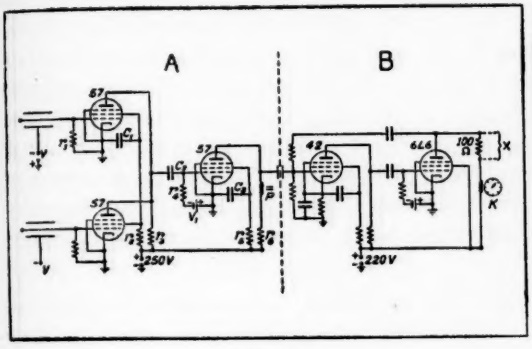

FIG. 1

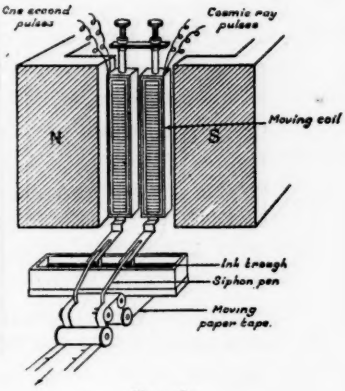

FIG. 2

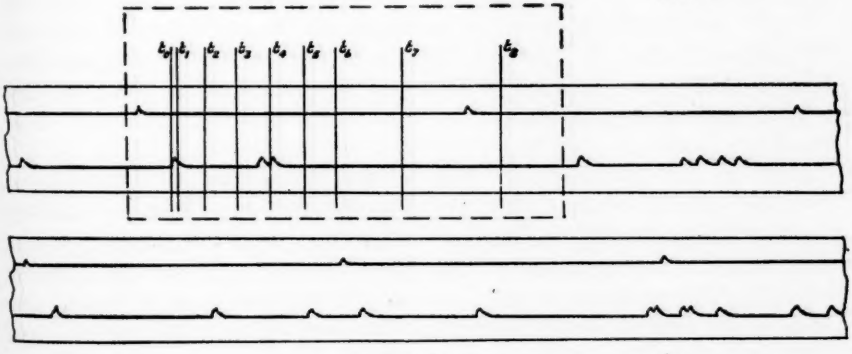

FIG. 3

FIG. 1. Circuit diagram showing A, the double coincidence set and amplifier operating the chronograph pen P; and B, the multivibrator working the telephone call counter K. X shows the points to which the coil of P was first connected. The constants are $r_1=10$ meg. Ω, $r_2=75000\,\Omega$, $r_3=100000\,\Omega$, $r_4=250000\,\Omega$, $r_5=50000\,\Omega$, $r_6=12000\,\Omega$, $C_1=\cdot05\,\mu$F, $C_2=\cdot5\,\mu$F, and $C_3=\cdot02\,\mu$F.

FIG. 2. Diagram of Chronograph recorder.

FIG. 3. Typical tape record of cosmic ray and one second pulses. Scale for making Marsden-Barratt analysis is also shown (Actual size).

A diagrammatical view of the chronograph recording device is shown in Fig. 2. Two moving coils are sensitively suspended in a strong magnetic

field produced by a permanent magnet. Each coil bears an arm at the lower end, and special capillary pens are attached by wax to these arms. The pens dip at one end in a small trough filled with ink and rest on a moving paper tape drawn at a uniform rate past them by an electric motor. The pressure of the pens on the paper could be adjusted by the moving coil suspension screws. The motor was operated from a battery set, and during the experiment the speed remained constant to within 2%. The speed of the moving tape could be easily changed by shifting the gears attached to the motor. The speed was adjusted after taking into consideration the counting rate and the likely duration of each particular experiment. One of the pens was made to register the arrival of cosmic rays as already described before. The other pen simultaneously marked uniform pulses arriving at intervals of 1 second. These pulses were obtained from a synchronous clock operated by a 1000 cycle standard valve maintained tuning fork. The time scale given by this arrangement was of an accuracy for surpassing that achieved in the rest of the experiment.

Fig. 3 shows a portion of a typical record. The resolving time of the pen as estimated from a record of uniform pulses fed from a pulse generator came to about 1/60th of a second. This value only forms a rough estimation, and hence it has not been used in the comparison of experimental data with theory. The length of the tape corresponding to one second in time was determined separately for each experiment by measuring accurately the lengths of a known interval of time at a number of places along the tape record, and taking a mean.

4. *Marsden-Barratt Analysis*

For making a Marsden-Barratt analysis of the tape record, a scale was made as shown in Fig. 3; having vertical lines ruled at distances from a fixed index line corresponding to certain fractions t_1, t_2 ····· of a second. The lines were ruled on the emulsion side of a transparent photographic plate with a fine needle fixed in a microtome; and the scratches were made more visible by rubbing rouge into them. After ruling, the distances between the various lines and the index line were again accurately measured to better than 1% accuracy. Thus the scale was marked out into different regions 1, 2, · · · etc., corresponding to various time intervals t_1, t_2 · · · etc. from the index line t_o. The procedure then consisted in placing the tape under the scale so that one particular cosmic ray pulse coincided with line t_o. If the next pulse was in the region between, say, lines t_4 and t_3, it was noted down as having belonged to group 4, *i.e.* of duration from between t_3 and t_4 seconds. The penultimate pulse was then made to coincide with t_0, and the

time interval between the two pulses was similarly noted into the appropriate group. In this way the intervals between the arrivals of the cosmic ray particles were classified into one or other of nine groups, the last group containing intervals larger than t_8.

There are however two difficulties in this method of analysis. One is the inaccuracy of making a pulse on the tape exactly coincide with the vertical index line on the scale. Then again the second pulse may not lie in between the lines bordering any range but might fall just on one particular line. A decision has then to be made whether the interval lies in the range to the right or to the left of the line in question. Though perhaps this might be expected to introduce considerable inaccuracies in tabulation, specially when the sizes of some of the small ranges are only about a millimetre in length; it is possible with the help of a reading lens, and a suitable convention for deciding ambiguous cases to arrive at surprisingly consistent results. An estimate can be formed of the extent of inaccuracy that can thus be introduced by considering the thickness of the lines on the scale; and it would be safe to put a value of 5% as the upper limit for the error in the smallest ranges. The second difficulty arises when two cosmic ray arrivals come so close to each other that the pen mark no longer shows two distinct deflections. It was found however, that the shape of the deflection showed a marked change even when two arrivals followed so closely that the pen had not been fully deflected after the first arrival. But such an estimation, though possible, would introduce considerable errors. It was therefore decided to draw the t_1 line of the scale at just such a distance from t_0 that all particles that would lie in group 2 (between t_1 and t_2) would be unambiguously resolved; which amounted to the condition that the distance between t_0 and t_1 should be just larger than the distance between the start of a deflection and the position of its peak.* All particles that lay in group 1 were noted but not taken into consideration for the final comparison of experimental data with theory. In the particular experiment where double coincidences due to cosmic rays were measured, a further complication was introduced by the fact that though a majority of the deflections were similar and of equal magnitude, there were in between a not inconsiderable number of deflections of varying sizes. These latter were attributed to false coincidences, and it was legitimate to assume that their occurrence was due to two independent arrivals striking individually the separate counter trays within the resolving time of the coincidence discriminating circuit. Hence in the analysis of this record a further convention had to be made; namely

* In Expt. 1, this practice was not carried out and t_1 was taken as equal to half t_2.

that we should neglect all deflections smaller than an arbitrary fixed magnitude, which was taken as just less than the height of the majority of deflections attributed to true coincidences.

The data so obtained directly gives us the total number of intervals which lie in the groups 1, 2 · · · 9, *i.e.* which had a duration between t_r to t_1, t_1 to t_2 · · · and t_8 to ∞ (t_r being the resolving time of the pen, naturally forms the lower limit for the measurement of time intervals). From this we can immediately calculate the number N_s of intervals larger than any particular t_s. This data collected for the several experiments is shown in Tables I and II. The first column indicates the groups that were excluded in order to arrive at N_s; and under the column 't_s seconds' is given the value of the corresponding 't_s'. The logarithm of N_s is also given and is plotted against t_s in Fig. 4. As explained earlier the curves should be linear. But to make a proper comparison with the theoretical expression (4), we need to know the value of the total number of intervals N_0 that would have been recorded had the resolving time of the apparatus been not t_r, but infinitely smaller. It is of course possible to extrapolate N_0 from any set of values N_s, t_s by assuming that the theoretical law (4) is valid. As however the resolving time t_r is not accurately known, the extrapolation from the 1st group would not be accurate. This group was therefore excluded and the mean N_0 was calculated from the extrapolated values obtained from all the other sets of N_s and t_s, as explained below.

TABLE I

Group	Expt. 1			Expt. 2		
	t_s sec.	N_s	log N_s	t_s sec.	N_s	log N_s
r*	·0166	8688	3·9389	·0166	9653	3·9847
1	·0510	8013	3·9038	·0208	8908	3·9498
2	·1021	7122	3·8526	·1022	6168	3·7902
3	·2042	5747	3·7594	·2044	3922	3·5935
4	·3063	4688	3·6710	·3070	2463	3·3915
5	·4084	3754	3·5745	·4095	1564	3·1942
6	·5105	3008	3·4783	·5113	982	2·9921
7	·7147	1944	3·2887	·7161	401	2·6031
8	1·021	1018	3·0077	1·023	125	2·0899

	t_s sec.	log N_s (theo.)	t_s sec.	log N_s (theo.)
Theoretical Values from eq. (4) ..	0	3·9533	0	3·9929
	·3	3·6747	·3	3·4152
	·6	3·3961	·6	2·8374

TABLE II

Group	Expt. 3			Expt. 4		
	t_s sec.	N_s	log N_s	t_s sec.	N_s	log N_s
r*	·0166	9234	3·9654	·0166	9028	3·9556
1	·0211	8677	3·9384	·0244	8516	3·9302
2	·1037	6270	3·7973	·1014	6955	3·8423
3	·2074	4216	3·6249	·2030	5394	3·7319
4	·3113	2781	3·4442	·3062	4153	3·6184
5	·4153	1856	3·2686	·4073	3263	3·5136
6	·5186	1253	3·0979	·5094	2517	3·4009
7	·7263	559	2·7474	·7137	1517	3·1810
8	1·0371	163	2·2122	1·0244	685	2·8357

	t_s secs.	log N_s (theo.)	t_s sec.	log N_s (theo.)
Theoretical Values ..	0	3·9812	0	3·9519
From eq. ..	·3	3·4703	·3	3·6279
(4) ..	·6	2·9594	·6	3·3040

TABLE III

t_s	Expt. 1		Expt. 2		Expt. 3		Expt. 4	
	R_s	R_0	R_s	R_0	R_s	R_0	R_s	R_0
t_1 ..	114·5	127·5	241·0	264·0	213·2	231·2	141·9	150·8
t_2 ..	101·7	126·2	166·9	259·2	154·1	229·0	115·9	149·4
t_3 ..	82·4	126·9	106·1	242·0	103·6	228·5	89·9	148·6
t_4 ..	67·0	129·9	66·6	281·5	68·3	249·0	69·2	145·6
t_5 ..	53·6	129·0	42·3	273·2	45·6	239·5	54·4	148·0
t_6 ..	43·0	130·4	26·6	273·8	30·8	235·5	41·9	150·2
t_7 ..	27·8	128·7	10·8	269·0	13·7	234·5	25·3	149·3
t_8 ..	14·5	127·9	..	..	..	..	11·4	151·6
Mean R_0	128·3		266·1		235·3		149·2	
Total Time Minutes	70		36·97		40·70		60	
N_0	8981		9838		9577		8951	
$\bar{T}$. secs.	·4676		·2255		·2550		·4022	

By dividing in any particular experiment the values of N_s by the total time T_s of the experiment, we arrive at the corresponding values for R_s, the rate per minute of intervals larger than t_s. Values for R_s are tabulated

in Table III for each experiment. Now, eq. (4) can be written in terms of R_s as

$$\log R_s = \log R_0 - \frac{t_s}{T} \log e.$$

But as $T = \frac{60}{R_0}$ seconds, we have the identity

$$\log R_0 - \log R_s = \frac{R_0}{60} t_s \log e. \qquad (5)$$

The solution for R_0 for any particular set R_0, t_s is easily found graphically by plotting separately the two sides of this equation against R_0. The extrapolated value in each case is given in Table III under column R_0. From the mean of R_0, we can immediately get N_0 and the true value of the mean interval $\overline{T}$. Both these quantities should to a large extent be free from errors of finite sampling. These values of N_0 and $\overline{T}$ have been used in eq. (4) to get the theoretical log. N_t as tabulated in Tables I and II; and these theoretical values for each experiment have been drawn as continuous lines in Fig. 4 for direct comparison with the experimental points. The consistency of the value of R_0 obtained from the different values of R_s is itself a good indication as to how far the distribution obeys the random law expressed by eq. (4). Fig. 5 shows the variation of both R_0 and R_s against t_s. While theoretically R_0 should remain constant, the value of R_s should diminish exponentially.

5. *Experimental Results*

The investigation of the time distribution of cosmic rays was carried out in three different experiments; while a fourth experiment was undertaken to verify whether it was possible to confirm with the same apparatus and under almost similar conditions the distribution of time intervals for a radioactive source. The various experiments were:—

(1) *Experiment* 1.—Cosmic ray investigation with a small Geiger counter having a cylinder 4 inches long, operating singly. The counting rate per minute was 128·3. The speed of the chronograph tape was 2·496 cm. sec.$^{-1}$

(2) *Experiment* 2.—Cosmic ray investigation with a large counter having a cylinder 8 inches long, operating singly. The counting rate per minute was 266·1. The speed of the chronograph tape was 4·858 cm. sec.$^{-1}$

(3) *Experiment* 3.—γ-Ray investigation with a midget Geiger counter having a cylinder 1 inch long. The background count of the counter was 23·7 and this was increased by a radioactive thorium source to 235·3 counts per minute. The speed of the chronograph tape was 4·779 cm. sec.$^{-1}$

(4) *Experiment* 4.—Cosmic ray investigation with a double coincidence Geiger-counter arrangement. Four counters having cylinders 12 inches long, were stacked two over two; and coincidences between the upper and the lower pairs were registered. With the very wide solid angle subtended by this arrangement, and a sensitive area of about 25 sq. inches for each pair, it was possible to get a counting rate of 149·2 counts per minute. The speed of the chronograph tape was 2·994 cm. sec.$^{-1}$

The proper functioning of the apparatus in each experiment was checked by noting during the Marsden-Barratt analysis, the number of cosmic ray intervals that successively occurred in a certain fixed time period, say 10 minutes. The fluctuations of the number of these intervals about the mean number expected in the same time period, give us an indication as to whether the experimental conditions remained constant during the run. If there is no variation in the efficiency of the apparatus, then the probable error calculated from the residuals should be smaller than the probable error taken from the total number of counts. This condition was well satisfied in each of the four experiments; showing that there was consistency not only in the functioning of the apparatus but also in the system of analysis with the scale.

A glance at Figs. 4 and 5 immediately makes it obvious that judged from all the criteria discussed before, the time distribution of cosmic rays as investigated in Experiments 1 and 4 agrees remarkably well with what we should expect from the random law. The very good fit with theory for the double coincidence experiment is specially significant, as we have here a detecting device sensitive only to cosmic rays as against terrestrial radioactive sources. For both experiments, what little variation there is in the value of the extrapolated R_0 (this amounts to 2% for the largest deviation from the mean) can be explained entirely by the estimated experimental error. In Experiment 2 however the fit between experimental points and the theory is not so good. Whether or not this deviation has any physical significance can be judged by considering the results in relation to those obtained in Experiment 3. The experimental conditions in these two experiments correspond closely to each other as far as the counting rate and the speed of the chronograph tape are concerned; and the same scale was used for making the Marsden-Barratt analysis in both cases. But while in Experiment 2 the counting rate was predominantly due to cosmic rays, in Experiment 3 the conditions were reversed so that cosmic rays only played a negligible role and the measured rate was mostly due to radioactivity. A comparison of the results of these two experiments therefore directly indicates the position in cosmic rays *vis-a-vis* radioactivity. It is important

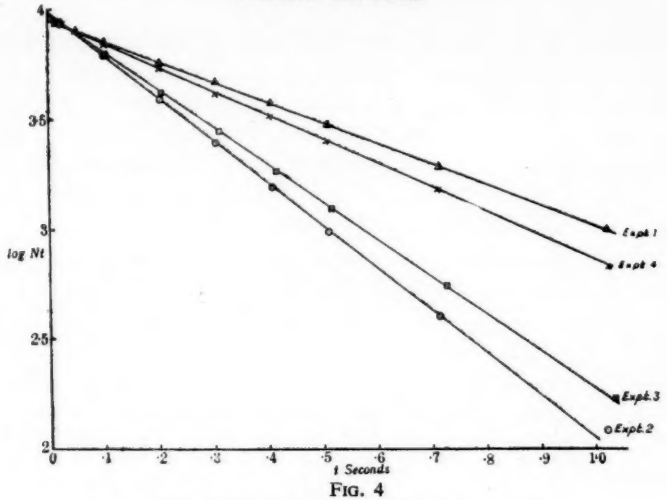

FIG. 4

△ Expt. points for cosmic rays with small counter.
⊙ ,, cosmic rays with large counter.
⊡ ,, radio-activity with Midget counter.
× ,, cosmic rays. Double coincidences.

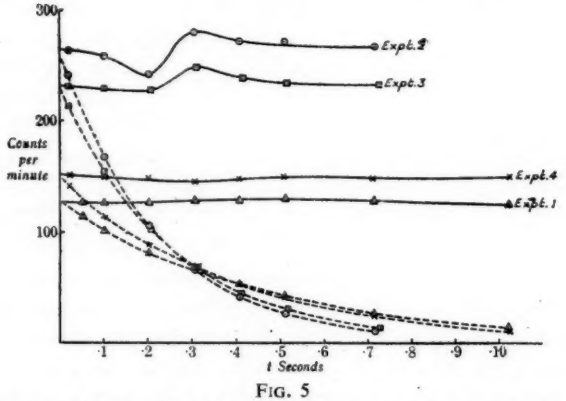

FIG. 5

Curves showing variation of R_s (dashed curves) and of the extrapolated values of R_0 (continuous lines).

to notice that for these two experiments the curves showing the variations in R_0 follow the same general trend; and indeed the maximum deviation from the mean R_0 occurs in both cases at t_4 and amounts to 6%. Though the magnitude of the error is slightly larger than what would be estimated from experimental inaccuracy, it is highly probable that it is due to some

peculiarity of the scale, possibly the ruling of the particular line t_4. Besides, the all round poorer fit with theory for these experiments is very probably due to the higher counting rates used. But in so far as this is present for both these experiments, it is justifiable to say that the lack of agreement is not due to any departure in the cosmic rays from the random law.

6. *Bateman Analysis*

A confirmatory check of the results obtained above was made by means of Bateman analysis of the chronograph tape records of all the four experiments. The number 'f' of intervals of some fixed duration 't' having 'n' particles in each of them, was found for various values of 'n'. This only required the counting of the number of cosmic ray pulses in successive intervals of 't' seconds as indicated by the one second pulses on the tape. No attempt was made to artificially eliminate the very small intervals where only a change in the shape of the deflection had occurred. The results of the analysis therefore cannot be taken as very accurate for the small ranges. In the case of Experiment 4 however, the same convention regard-

TABLE IV

n	f			
	Expt. 1	Expt. 2	Expt. 3	Expt. 4
1	1	0	0	5
2	9	0	0	27
3	17	0	7	59
4	48	3	11	110
5	79	3	6	152
6	139	5	33	205
7	177	22	59	221
8	172	39	64	179
9	122	46	73	143
10	124	72	92	105
11	95	78	86	75
12	74	82	94	36
13	41	102	72	32
14	31	91	44	10
15	18	74	44	4
16	15	62	36	1
17	7	45	21	3
18	3	28	14	0
19	1	19	6	0
20	4	13	4	0
21	0	3	2	0
22	0	3	1	0
23	0	1	0	0
t	4 secs.	3 secs.	3 secs.	3 secs.
Σf	1177	791	769	1367
Σnf	10236	10243	8524	9922
$\Sigma n^2 f$	98502	141025	103264	81602
Q^2	0·928	1·03	0·817	0·966

ing the elimination of small deflections (due to false coincidences) was adopted as in the Marsden-Barratt analysis.

The results of the analysis are presented in Table IV for all the four experiments. The mean number of particles $\bar{n}$ that arrive in the interval 't' is obtained by dividing the total number of particles Σnf by the total number of intervals Σf. But the square of the standard deviation is:—

$$6^2 = \frac{\Sigma f\,(n-\bar{n})^2}{\Sigma f} = \frac{\Sigma f n^2}{\Sigma f} - \bar{n}^2$$

Hence dividing by $\bar{n} = \frac{\Sigma fn}{\Sigma f}$ we get

$$Q^2 = \frac{\Sigma fn^2}{\Sigma fn} - \frac{\Sigma fn}{\Sigma f}.$$

The values of Q^2 are tabulated for each experiment. Experiments 2 and 4 show a normal distribution as the deviation of the value of Q^2 from unity is small and may easily be due to errors of random sampling. Experiments 1 and 3 show slightly sub-normal distributions; and this is very probably due to the errors in the marking of small intervals as already explained before. The number of small time intervals must obviously have been overestimated; and in any case, as this has happened to the largest degree in the experiment on radioactivity, no importance need be attached to this subnormality for the purpose of our investigation.

7. *Discussion*

The time distribution of any radiation depends basically on the mechanism by which the emission takes place. The random law as we observe it in the case of nuclear phenomenon is only an expression of the fact that every atom in a radioactive material has the same chance to disintegrate. However it is well known that when a chain of radioactive elements has a member with a short life time, comparable to the time intervals experimentally measured, a departure from the time randomness is in fact observed. Indeed a good way of detecting the existence of a short life product is by studying the time distribution of the emitted radiation. But such departures from time-randomness can only be studied by observing the total emitted radiation, so that the space randomness does not mask the effect.

While the origin and the mechanism of the production of cosmic rays is still a matter of conjecture, it is not possible to anticipate what would be the time distribution in a primary beam of radiation. Even if there were any departures from time randomness in this beam, it is very likely that in any terrestrial measurement of the distribution, the effect would be completely masked by space randomness. However we do know that there are

numerous processes by which secondary particles are produced in our atmosphere by the primary beam of cosmic rays. Whenever such a production takes place at high energy, the product or products have a great tendency to keep the original direction of the primary particle without suffering much angular divergence. In such a case we would be able to register not only one, but several related particles in the same detecting device, provided the exposed sensitive area of the latter is large enough. The time difference in the arrivals of these related particles (and we need not assume that the primary particle must be absent from the group) depends on the distance from the detector at which the particles are produced, and the individual velocities of the particles. Considering the high velocities of the majority of cosmic ray particles (electrons, positrons and mesons), it is not likely that the time difference would be large if the production of secondary radiation can take place only in our own atmosphere. The interval would be probably of the order of microseconds, and hence quite outside the range of the present investigation. For heavier particles like the neutron, a larger time interval might be expected because of the much lower velocities compared with those of electrons and mesons. To detect such an effect, it would be necessary to use not the ordinary Geiger counter but an apparatus sensitive to both slow neutrons and the high energy ionising component of the cosmic radiation.

The very good agreement between the experimental and theoretical time distribution of cosmic rays as investigated here, certainly goes to show that upto intervals as small as one-fiftieth of a second, there is no appreciable lack of time randomness of the radiation. The size of the detecting area also seems to have no effect on the extent of agreement. It might nevertheless be worthwhile to investigate the time distribution for much smaller intervals using an electrical time interval meter like the one developed by Roberts. The use of a much larger sensitive area, having a bias for the vertical direction of incidence would also help in detecting any deviation, if indeed it does exist.

In conclusion it is a pleasure to acknowledge the unfailing support and guidance that Prof. Sir C. V. Raman has given throughout this investigation. I am deeply grateful to Prof. K. Aston for having whole-heartedly placed at my disposal the chronograph recording device without which the investigation would have been impossible.

8. *Summary*

An experimental test of the time distribution of cosmic rays has been made using different Geiger counter arrangements. The distribution given

by cosmic rays has been compared with that due to radioactivity. It is found that at least upto the small time intervals ($\frac{1}{50}$ sec.) reached in the experiment, the arrivals of cosmic rays follow a law to be expected from complete time randomness; and their behaviour is therefore similar to that shown by radiations from radioactive sources. The possibility of detecting deviations from time randomness in the case of cosmic rays has been discussed.

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THE THEORY OF PARTICLES OF SPIN HALF AND THE COMPTON EFFECT

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It is generally accepted that the Dirac equation correctly describes the behaviour of a particle of spin half $\hbar$. However, the theory is definitely untenable in its original form since it also allows a free particle to exist in states of negative mass and energy, and particles of this type are not known in nature. We will call this formulation of the theory the " original " Dirac theory for brevity. Dirac removed the difficulty by the addition of the assumption that all the negative energy states are normally filled in nature each with one particle. Together with the further necessary assumption that the particles obey the Pauli exclusion principle this stops an actual particle in a positive energy state from jumping into a negative energy state. As is well known, this assumption leads at once to the conclusion that particles must appear in nature like the original particle but with the opposite electric charge, and that such a particle and an electron must be capable of being created in pairs. The existence of the positron, and the observed process of pair creation are considered as two of the most successful predictions of this formulation of the theory, which we will call the ' hole ' theory for brevity. It also provides the long looked for reason why particles of spin half must obey the Pauli exclusion principle.

Now a large number of very common processes in nature take place as second order processes in two steps by way of an intermediate state, and it is generally considered to have been demonstrated that the ' original ' Dirac theory and the ' hole ' theory lead to the same probabilities for these. The purpose of this paper is to show that in our opinion this demonstration is fallacious. Indeed, Weisskopf (1934) has already shown that the transverse self-energy of an electron is different in the two theories, but since the self-energy is infinite in either theory, although to a different degree, not much attention has been paid to this point.

The demonstration that the original Dirac theory and the hole theory give the same probabilities for all second order processes is mainly the following. In the original theory, one of the ways by which the double transition can take place is that in which the existing particle jumps into an

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intermediate state of negative energy, jumping in the next step to the final state of positive energy. On the hole theory the first jump cannot take place by the exclusion principle since the negative energy state is already occupied by one particle. The process therefore takes place in the following way. The particle in the state of negative energy jumps first to the final state of positive energy, the matrix element for this process being the same as that of the second jump in the original theory. After this, the initial particle jumps into the vacant negative energy state, the matrix element for this being the same as that of the first jump on the original theory. Thus the products of the two matrix elements for the two steps are the same in both theories, and on this ground it has been concluded that the two theories lead to the same probability for the second order process. This argument, in our opinion, appears to overlook the fact that the energy denominators in the second order perturbation formula for the process are not the same in the two theories. In the original theory the particle jumps from a positive to a negative energy state, so that the difference in energy between the initial and intermediate states of the system as a whole is positive. In the hole theory, the particle in the negative energy state jumps to a state of positive energy, so that the difference in energy between the initial and intermediate states of the system as a whole is negative, corresponding to the existence of an electron pair besides the initial electron in the intermediate state. It follows from this that the final probability for any second order process will not be the same on the two theories. Indeed, the difference on the two theories in the transverse self-energy of the electron, referred to above, comes precisely from the difference in the energy denominators in the two cases.

In this paper we shall illustrate the above argument by investigating two physical processes in detail. The first is the scattering of light by a free electron. This process is of particular interest because the Compton effect has been studied experimentally in considerable detail, and the experiments appear to fit the Klein-Nishina formula very well. This formula gives the scattering of light by a free electron as derived from the original Dirac theory. Contrary to what is generally believed, the hole theory gives a formula different from this which is calculated in the next section. The two formulæ agree when the energy of the light quantum is small compared with the electron mass, for then they both reduce to the classical Thomson formula. For quanta of energy comparable with, or larger than, the electron mass, there is considerable difference between the two, the total cross-section being considerably larger on the new formula. For these high energies, however, the angular distribution of the scattering has not been investigated

experimentally with any great accuracy. On the other hand the total scattering cross-section for radiation of 2·6 M.e.V. energy as measured by Meitner and Hupfeld (1930) appears to agree very well with the Klein-Nishina formula and is in definite disagreement with the new formula. Now the hole theory is the only form in which the Dirac theory is logically tenable, and it appears to give at least qualitative, and perhaps quantitative, agreement with experiment in its description of processes involving the creation of positrons. Its definite disagreement with experiments on the Compton effect therefore creates very great difficulties, the solution of which is not clear to us.

The other process which is investigated in detail is the scattering of charged transversely polarized mesons by neutrons or protons on the usual formulation which does not assume the existence of doubly charged protons. The proton or neutron is assumed to obey the Dirac equation. This process is very similar theoretically to the Compton effect discussed above. The only difference is that due to the charge of the meson, there are now only two intermediate states instead of the four in the Compton effect, and this brings out some of the differences between the scattering on the original Dirac theory and the hole theory more clearly.

There are several other important processes which will be quantitatively different on the hole theory to what they are on the original Dirac theory, as for example the radiation loss of electrons and the pair creation by quanta. Indeed, the former is intimately connected with the scattering of light by a free electron, as has been shown by Weizsäcker (1934). The discussion of these will be left to a later paper.

The scattering of light by a free electron

Assume the electron to be initially at rest. Let the incident quantum have a momentum $\mathbf{k}_0$ and the scattered quantum a momentum $\mathbf{k}$, the momentum of the electron after the impact being $\mathbf{p}$, given by

$$\mathbf{k}_0 = \mathbf{k} + \mathbf{p}. \tag{1}$$

Let the final energy of the electron be $E = \sqrt{p^2 + m^2}$, m being the electron mass. (The velocity of light is put equal to unity.) Then

$$k_0 + m = k + E \tag{2}$$

whence, in conjunction with (1)

$$k = \frac{k_0 m}{m + k_0(1 - \cos\theta)} = \frac{k_0}{1 + \gamma(1 - \cos\theta)}, \tag{3}$$

where $\gamma = \frac{k_0}{m}$ and θ is the angle through which the quantum is scattered.

Let ϵ_0 be a unit vector in the direction of polarization of the incident quantum so that $(\epsilon_0, \mathbf{k}_0) = 0$, and ϵ that in the direction of polarization of the scattered quantum, so that $(\epsilon, \mathbf{k}) = 0$. The probability for the transition of the system from the initial state i to the final state f per unit time due to the interaction $\mathcal{J}$ is

$$w = \frac{2\pi}{\hbar} \left| \sum_m \frac{(f \mid \mathcal{J} \mid m)\,(m \mid \mathcal{J} \mid i)}{E_i - E_m} \right|^2 \rho_f, \tag{4}$$

where E_i and E_m are the energies of the system as a whole in the initial and intermediate states. ρ_f is the total number of final states of the whole system in the energy interval dE_f, E_f being the final energy of the whole system. For the scattering considered above [see Heitler (1936), p. 149]

$$\rho_f = \frac{E k^3}{m k_0} \frac{d\Omega}{(2\pi\hbar)^3}, \tag{5}$$

where $d\Omega$ is the solid angle into which the light quantum is scattered.

On the original Dirac theory, the process takes place through four intermediate states and may be represented schematically as

$$k_0 + e\,(0) \rightarrow \begin{matrix} \text{I} \\ \text{II} \\ \text{III} \\ \text{IV} \end{matrix} \left\{ \begin{matrix} e\,(\mathbf{k}_0) \\ [e\,(\mathbf{k}_0)] \\ k_0 + k + e\,(-\mathbf{k}) \\ k_0 + k + [e\,(-\mathbf{k})] \end{matrix} \right\} \rightarrow k + e\,(p) \tag{6}$$

where $e\,(\mathbf{k}_0)$ denotes an electron of momentum $\mathbf{k}_0$ and positive energy, while $[e\,(\mathbf{k}_0)]$ denotes an electron of the same momentum in a state of negative energy. The energy of the electron in the intermediate state I is

$$E' \equiv + \sqrt{m^2 + k_0^2} \tag{7}$$

and in the intermediate state III

$$E'' \equiv + \sqrt{m^2 + k^2}. \tag{8}$$

In the intermediate states II and IV it is $-E'$ and $-E''$ respectively.

On the hole theory the same process is represented by the following scheme.

$$\begin{matrix} k_0 + e\,(o) \\ + [e\,(\mathbf{k}_0)] \\ + [e\,(-\mathbf{k})] \end{matrix} \rightarrow \begin{matrix} \text{I} \\ \text{II}' \\ \text{III} \\ \text{IV}' \end{matrix} \left\{ \begin{matrix} e\,(\mathbf{k}_0) + [e\,(\mathbf{k}_0)] + [e\,(-\mathbf{k})] \\ k_0 + e\,(o) + k + e\,(\mathbf{p}) + [e\,(-\mathbf{k})] \\ k_0 + k + e\,(-\mathbf{k}) + [e\,(\mathbf{k}_0)] + [e\,(-\mathbf{k})] \\ e\,(o) + [e\,(\mathbf{k}_0)] + e\,(\mathbf{p}) \end{matrix} \right\} \rightarrow \begin{matrix} k + e\,(\mathbf{p}) \\ + [e\,(\mathbf{k}_0)] \\ + [e\,(-\mathbf{k})] \end{matrix} \tag{9}$$

$[e\,(\mathbf{k}_0)]$ and $[e\,(-\mathbf{k})]$ are the two electrons occupying the two states of negative energy concerned. They are initially and finally not observable, but in the intermediate states II′ and IV′ the states they vacate appear as

positrons of momentum $-\mathbf{k}_0$ and $\mathbf{k}$ respectively. The transitions *via* the intermediate states I and III are identical in the schemes (6) and (9). The transitions *via* the states II and IV in (6) are replaced by II′ and IV′ in (9).

For the transition *via* the second intermediate state in (6) we must insert for $E_i - E_m$ in formula (4)

$$E_i - E_{II} = k_0 + m + E' \tag{10}$$

whereas for the corresponding transition *via* the state II′ in (9) we have

$$E_i - E_{II'} = -E' - k - E = -(k_0 + m + E') \tag{11}$$

by (2). Similarly

$$E_i - E_{IV} = m - k + E'', \tag{12}$$

while

$$E_i - E_{IV'} = k_0 - E'' - E = -(m - k + E'') \tag{13}$$

by (2).

Now substituting (5) in (4) and putting in the expressions for the matrix elements (see, for example, Heitler, 1936, p. 149) the differential effective cross-section $d\phi$ for the scattering process becomes

$$d\phi = e^4 \frac{Ek^2}{mk_0^2} \left| \Sigma \left[\frac{(\bar{u}_E \alpha u_{E'})(\bar{u}_{E'} \alpha_0 u_m)}{m + k_0 - E'} \pm \frac{(\bar{u}_E \alpha u_{-E'})(\bar{u}_{-E'} \alpha_0 u_m)}{m + k_0 + E'} \right.\right.$$
$$\left.\left. + \frac{(\bar{u}_E \alpha_0 u_{E''})(\bar{u}_{E''} \alpha u_m)}{m - k - E''} \pm \frac{(\bar{u}_E \alpha_0 u_{-E''})(\bar{u}_{-E''} \alpha u_m)}{m - k + E''} \right] \right|^2 d\Omega. \tag{14}$$

Here $u_{E'}$ represents, for example, a matrix of one column and four rows giving the solution of the Dirac equation for a free particle of energy E' and momentum $\mathbf{k}_0$, while $u_{-E'}$ represents the corresponding solution for a free particle of energy $-E'$ and momentum $\mathbf{k}_0$. As usual α_1, α_2, α_3 and β are the four Dirac matrices and

$$\left.\begin{aligned} \alpha_0 &\equiv (\alpha,\ \epsilon_0) \\ \alpha &\equiv (\alpha,\ \epsilon) \end{aligned}\right\} \tag{15}$$

The positive signs in front of the second and fourth terms in (14) have to be taken on the original theory in view of (10) and (12), whereas on the hole theory (11) and (13) show that the negative signs have to be taken. The summation is only over the two states of spin for each energy and momentum. It is obvious from (14) that the original theory and the hole theory give different cross-sections for the same process.

It is well known that for $k_0 \ll m$ the main contribution to the scattering comes from the transitions to the intermediate states of negative energy, the positive energy intermediate states contributing little. Hence, for $k_0 \ll m$, the first and third terms are negligible compared with the second and fourth

so that the change in sign of these terms does not affect (14). Therefore, for $k_0 \ll m$, the new formula approximates closely to the Klein-Nishina formula, and in the limit $k \to 0$ both reduce to the classical Thomson formula. The difference between the new formula and the Klein-Nishina formula only appears at higher energies where the first and third terms in (14) also make an appreciable contribution, so that the change in sign of the second and fourth terms affects the magnitude of the cross-section.

Henceforth we restrict ourselves to calculating (14) with the negative sign in front of the second and fourth terms for this is the correct cross-section given by the hole theory. Consider the first two terms in (14). The summation over the two states of spin of the intermediate states gives as usual

$$\frac{(\bar{u}_E\, \alpha \{E' + (\boldsymbol{\alpha}, \mathbf{k}_0) + \beta m\}\, \alpha_0\, u_m)}{2\, E'\, (m + k_0 - E')} - \frac{(\bar{u}_E\, \alpha \{E' - (\boldsymbol{\alpha}, \mathbf{k}_0) - \beta m\}\, \alpha_0\, u_m)}{2\, E'\, (m + k_0 + E')},$$

which may be brought to a common denominator and written

$$\frac{(\bar{u}_E\, \alpha\, K_1\, \alpha_0\, u_m)}{2\, m\, k_0\, E'} \tag{16}$$

where

$$K_1 = (m + k_0)\, (\boldsymbol{\alpha}, \mathbf{k}_0) + k_0\, (k_0 - m) - m\, (m + k_0)\, (1 + \beta), \tag{17}$$

since by (7)

$$(m + k_0)^2 - E'^2 = 2\, m\, k_0.$$

Similarly, the third and fourth terms in (14), after summing over the spin of the intermediate states lead to

$$-\frac{(\bar{u}_E\, \alpha_0\, K_2\, \alpha\, u_m)}{2\, m\, k\, E''}, \tag{18}$$

where

$$K_2 = (k - m)\, (\boldsymbol{\alpha}, \mathbf{k}) + k\, (m + k) - m\, (k - m)\, (1 + \beta), \tag{19}$$

so that (14) reduces to

$$d\phi = \left(\frac{e^2}{m}\right)^2 \frac{E\, k^2}{4 m k_0^2} \left| \frac{(\bar{u}_E\, \alpha\, K_1\, \alpha_0\, u_m)}{k_0 E'} - \frac{(\bar{u}_E\, \alpha_0\, K_2\, \alpha\, u_m)}{k E''} \right|^2 d\Omega. \tag{20}$$

Summing over the spin of the final state and averaging over the spin of the initial state we get finally

$$d\phi = \left(\frac{e^2}{m}\right)^2 \frac{k^2}{4 m k_0^2} \left[2m + k_0 - k + \frac{k_0^2 - m^2}{k_0 E'^2} \left\{ 2\, (\boldsymbol{\epsilon}, \mathbf{k}_0)^2 + (\mathbf{k}, \mathbf{k}_0) \right\} \right.$$

$$- \frac{k^2 - m^2}{k E''^2} \left\{ 2\, (\boldsymbol{\epsilon}_0, \mathbf{k})^2 + (\mathbf{k}, \mathbf{k}_0) \right\}$$

$$\left. + \frac{1}{k\, k_0 E' E''} \left(\left\{ 1 - 2\, (\boldsymbol{\epsilon}_0, \boldsymbol{\epsilon}) \right\} \left\{ 2 m k\, k_0 (k + m)(k_0 - m) - 8 m^2\, k\, k_0 (k_0 - k) \right. \right. \right.$$

$$+ 2m^3 (k_0 - k)^2\Big\} + 2(\epsilon, \mathbf{k}_0)^2 k(k+m)(k_0+m)$$
$$- 2(\epsilon_0, \mathbf{k})^2 k_0 (k_0 - m)(k - m)$$
$$+ 4m(\epsilon, \mathbf{k}_0)(\epsilon_0, \mathbf{k})(\epsilon_0, \epsilon)\Big\{2k k_0 - m(k_0 - k)\Big\}\Big)\Big] d\Omega. \quad (21)$$

The Klein-Nishina formula got by taking the positive signs in (14) is

$$d\phi_{\text{K.N.}} = \left(\frac{e^2}{m}\right)^2 \frac{k^2}{4k_0^2}\left[\frac{k_0}{k} + \frac{k}{k_0} - 2 + 4(\epsilon_0, \epsilon)\right] d\Omega. \quad (22)$$

If $k_0 \ll m$, then by (3), $k = k_0$ and both (21) and (22) reduce to

$$\left(\frac{e^2}{m}\right)^2 (\epsilon_0, \epsilon)^2 \, d\Omega, \quad (23)$$

which is the classical Thomson formula. For very small θ, neglecting quantities of the order θ^2, (21) reduces to

$$\left(\frac{e^2}{m}\right)^2 \left[(\epsilon_0, \epsilon)^2 + \frac{\gamma^2}{1+\gamma^2}\{1 - 2(\epsilon_0, \epsilon)^2\}\right] d\Omega \quad (24)$$

and hence even for these small angles, it does not reduce to the Thomson formula as the Klein-Nishina formula does, except when $\gamma \ll 1$. For quanta of momentum comparable with or larger than m, there is therefore a depolarization even for very small angles of scattering. Summing and averaging (21) over the two directions of polarization of the scattered and incident quantum respectively, it simplifies to

$$d\phi = \left(\frac{e^2}{m}\right)^2 \frac{k^2}{2mk_0^2}\Big[(k_0 - k + 2m) + \frac{k_0^2 - m^2}{E''}\{k\cos\theta - k_0 \sin^2\theta\}$$
$$- \frac{k^2 - m^2}{E''^2}\{k_0 \cos\theta + k \sin^2\theta\}$$
$$+ \frac{\sin^2\theta}{E'E''}\{k k_0 (k_0 - k) + m(k_0^2 + k^2) + m(k_0 - k)(k + m)\Big] d\Omega. \quad (25)$$

The total cross-section is got by integrating (25) over all scattering angles. Due to the appearance of E'' in the denominator, this leads to a very cumbersome expression.

$$\phi = \pi\left(\frac{e^2}{m}\right)^2 \Big[\Big(3\frac{\gamma^2+\gamma+1}{\gamma a^2} + \frac{\gamma^2+4\gamma+2}{\gamma^4 a^2}\Big)\log b^2 + 2\frac{\gamma^3+\gamma^2-2\gamma-1}{\gamma^4}\log\frac{a}{c}$$
$$- \frac{2(\gamma+1)^2}{\gamma b^4} - \frac{4\gamma^2}{a^2 b^4} - \frac{4(\gamma^2-1)}{\gamma a^2} + \frac{2(\gamma^2+3\gamma+2)}{\gamma^3}\tan^{-1}\frac{2\gamma^2}{(1+\gamma)^2}$$
$$+ \frac{1}{\gamma^2 a}\Big\{2\gamma^2 + 3\gamma - 5 - \frac{\gamma-3}{2\gamma^2}\Big\}\log\left(\frac{\gamma+a}{\gamma+c}\right) b^2$$
$$+ \frac{(\gamma+2)(\gamma^2+\gamma-1)}{\gamma^3 a}\log\frac{a-1}{c-b^2} - \frac{1}{\gamma^4}\Big(4\gamma^3+3\gamma^2-3\gamma-1\Big) + \frac{(4\gamma-3)(\gamma+1)}{2\gamma^3}$$
$$+ \frac{c}{a}\Big\{\frac{4\gamma^3+3\gamma^2-3\gamma-1}{\gamma^4 b^2} - \frac{\gamma-1}{2\gamma^3 b^2} - \frac{\gamma^2+\gamma-1}{\gamma^3}\Big\}\Big] \quad (26\,a)$$

where

$$a = \sqrt{\gamma^2+1}$$
$$b = \sqrt{2\gamma+1} \qquad (26\,b)$$
$$c = \sqrt{\gamma^2+(1+2\gamma)^2}.$$

For $\gamma \ll 1$ this simplifies to

$$\phi = \frac{8\pi}{3}\left(\frac{e^2}{m}\right)^2\left(1-2\gamma+\frac{641}{80}\gamma^2+\cdots\right). \qquad (27)$$

This is very similar to the corresponding limit of the Klein-Nishina formula, namely

$$\phi_{\text{K.N.}} = \frac{8\pi}{3}\left(\frac{e^2}{m}\right)^2\left(1-2\gamma+\frac{26}{5}\gamma^2+\cdots\right) \qquad (28)$$

For $\gamma \gg 1$, neglecting terms of higher order (26) becomes

$$\phi = 5\pi\left(\frac{e^2}{m}\right)^2\frac{\log 2\gamma}{\gamma}, \qquad (29)$$

which is precisely five times the corresponding limit of the Klein-Nishina formula.

The scattering of charged mesons by heavy particles

It is assumed as usual that the proton and neutron, being particles of spin half, obey the Dirac equation. To see more clearly the difference in the scattering on the original Dirac theory and the hole theory we investigate the scattering of a positively charged meson by a neutron, and assume for the purposes of this paper that the neutron may change into a proton by the absorption of the positive meson, but that no jumps to heavy particle states of negative and double charge are possible. Then, instead of the four intermediate states by which the scattering of the light quantum discussed above takes place, there are only two corresponding to the states I and II in (6) or I and II′ in (9).

In order to keep the parallel between this section and the previous section as close as possible, we assume that the meson has a spin 1 and consider the scattering of a transversely polarized meson to a final state in which it is also transversely polarized. We use the notation of a previous paper (Bhabha, 1938), in which the interaction of mesons with heavy particles is also given (formula 58*a*). It is here useful to consider the g_1 interaction* only, for the scattering by the g_2 interaction does not involve transitions to

*The value of g_1 in the previous paper is $\sqrt{4\pi\hbar^2c^2}$ times the value of g_1 in this paper. The definition of g_1 here adopted corresponds exactly to the definition of e in the previous section and gives g_1^2/r as the interaction between two heavy particles at a distance r.

negative energy in the non-relativistic approximation and the scattering due to it is the same on the original Dirac theory and the hole theory.

It is convenient to do the calculation in the centre of gravity system in which the meson has an initial momentum $\mathbf{p}_i$ and the neutron a momentum $-\mathbf{p}_i$. Denote the momentum of the scattered meson by $\mathbf{p}_i'$. The calculation follows very closely that given in the previous paper (Bhabha, 1938), and runs parallel to that of the preceding section. Denote the mass of the heavy particle by M, that of the meson by μ. Let $E_p \equiv \sqrt{p^2+\mu^2}$ and $E_N \equiv \sqrt{p^2+M^2}$ be the energies of the meson and neutron respectively. In the intermediate states I and II, the neutron turns into a proton at rest with energies M and $-M$ respectively. Summing over the two states of spin in the intermediate states, the differential effective cross-section for the scattering into the solid angle $d\omega$ is now

$$d\Phi = \frac{g_1^4 E_N^2}{4 E_i^2} \left| \frac{(\overline{u_N'} \alpha (1+\beta) \alpha_0 u_N)}{E_i - M} - \frac{(u_N' \alpha (1+\beta) \alpha_0 u_N)}{E_i + M} \right|^2 d\omega \qquad (30)$$

on the hole theory. On the original Dirac theory the minus sign before the second term would be replaced by a plus. $E_i \equiv E_N + E_p$. Summing and averaging over the two states of spin in the final and initial states of the neutron respectively (30) becomes

$$d\Phi = \frac{g_1^4}{4E_i^2}\left[\frac{(E_N - M)^2}{(E_i - M)^2} + \frac{(E_N + M)^2}{(E_i + M)^2} - \frac{2p^2 \cos\Theta}{E_i^2 - M^2}\right] d\omega, \qquad (31)$$

where Θ is the scattering angle in the centre of gravity system. The first two terms are the squares of the first and second terms in (30) respectively, and do not contain the scattering angle. The last term results from the cross product of the two terms in (30). The sign of this would therefore be reversed on the original Dirac theory. In the non-relativistic limit $p_i \to 0$, the second term in (31) which is entirely due to the second term in (30) dominates over the others. This clearly demonstrates the well-known circumstance mentioned earlier that in the non-relativistic limit the main contribution to the scattering comes from transitions to the intermediate states of negative energy. In the extreme relativistic case $p_i \gg M$, (29) simplifies to

$$d\Phi = \frac{1}{16}\left(\frac{g_1^2}{\mu}\right)^2 \left(\frac{\mu}{p_i}\right)^2 (1 - \cos\Theta)\, d\omega, \qquad (32)$$

On the original theory this is replaced by $(1 + \cos\theta)$. Thus, in the centre of gravity system the original theory and the hole theory give an entirely different angular distribution for the scattering, the scattering being forward in the original theory, backwards in the hole theory. The total

cross-section is however the same in both theories in this particular case, as an integration of (32) shows.

It should be noticed in passing that in the extreme relativistic case the above cross-section decreases inversely as the square of the momentum even for charged mesons, in agreement with the classical theory (Bhabha, 1939). This is because we have only considered the scattering of transversely polarized mesons into transversely polarized states. The cross-sections previously obtained which continued to increase as p_i^2 to the highest energies are due to transitions from and to *longitudinally* polarized meson states. In the classical theory and for neutral mesons in the quantum theory the scattering of longitudinally polarized mesons is actually less than that of transversely polarized mesons in the extreme relativistic case by a factor $(\mu/p_i)^2$. Thus the asymmetry due to the charge does not essentially affect the scattering of transversely polarized mesons to transverse states, but makes a vital difference between the scattering of charged and uncharged mesons to and from longitudinally polarized states. It is precisely this asymmetry which is removed by allowing the heavy particles to exist in states of all integral charges as suggested by one of us (Bhabha, 1940).

Discussion

As mentioned in the second section, the new formula (25) for the scattering of light by free electrons as derived strictly on the basis of the hole theory differs from the Klein-Nishina formula only for quanta of high energies. The highest energy for which accurate measurement of the angular distribution of the scattered intensity have been carried out is for $\gamma = 0{\cdot}173$ by Friedrich and Goldhaber (1927). Putting the scattering at 90° as 100, Table I gives the intensity as a function of angle. The second column gives the observed values, the third those derived from

TABLE I

Angular dependence of the scattered intensity for $\gamma \equiv k_0/m = 0{\cdot}173$
Observed values by Friedrich and Goldhaber

Scattering Angle	Observed Values	New Formula	Klein-Nishina
30°	243·4	242·4	257·5
60°	144·3	151·8	154·5
90°	100·0	100·0	100·0
120°	103·7	96·38	103·0
150°	138·7	111·5	124·5

(25)* and the fourth those from the Klein-Nishina formula. The marked deviation from the Thomson formula and the asymmetry in the forward direction are due to purely relativistic effects and result from transforming by the Lorentz transformation a symmetrical distribution in the system in which the quantum and electron have equal and opposite momenta to the system in which the electron is initially at rest. While the Klein-Nishina formula appears to agree somewhat better at large angles, the new formula is in better agreement at smaller scattering angles. The above experiment appears to be insufficient to decide between the new formula and the Klein-Nishina formula.

The angular distribution of the scattered intensity as given by both formulæ for higher energies is given in Table II. The figures show that the new formula gives more small angle and less large angle scattering than the

TABLE II

Angular dependence of the scattered intensity for different γ

Angle	$\gamma = 1$		$\gamma = 2$	
	New Formula	Klein-Nishina	New Formula	Klein-Nishina
30°	0·858	0·750	0·4562	0·2101
60°	0·522	0·250	0·1395	0·0353
90°	0·234	0·100	0·0429	0·0120
120°	0·101	0·075		0·0064
150°	0·054	0·075		
180°	0·034	0·075		

Klein-Nishina formula. This is however not generally true of the difference between the original Dirac theory and the hole theory. In the scattering of mesons investigated in the previous section, the hole theory gives less forward and more backward scattering than the original theory.

The figures for the total scattering cross-section given by (26) and the corresponding figures for the Klein-Nishina formula are given in Table III in units of the Thomson cross-section $\phi_0 = 8\pi e^4/3m^2$. Measurements of the total scattering of hard X-rays and γ-rays of different energies have been made by Read and Lauritsen (1934) and Tarrant (1930) and Meitner and Hupfeld (1930). All these observations are in very good agreement with

*The energy scattered per unit solid angle divided by the incident intensity is got by multiplying (25) by k/k_0. The figures given in Table II are this quantity in units $(e^2/m)^2$. In Table I they have been arbitrarily put equal to 100 at 90°.

the Klein-Nishina formula (see, for example, Heitler, 1936, p. 160). They are in definite disagreement with the new formula (26), which for the 5·1 m. γ-ray gives more than double the observed cross-section.

TABLE III

Total scattering cross-section in units of $\frac{8\pi}{3}\left(\frac{e^2}{m}\right)^2$

γ	Formula (26)	Klein-Nishina
1	0·77	0·43
5·1	0·51	0·19

We are therefore faced with a very paradoxical situation. The original Dirac theory gives a scattering of hard radiation by free electrons in good agreement with observation, but also allows the electron to behave in a way quite contrary to experience. It cannot explain the observed process of pair creation. On the other hand, the hole theory is undoubtedly more correct in that it predicts the existence of the positron and describes the process of pair creation correctly, at least qualitatively. It is however in definite quantitative disagreement with the scattering of hard radiation by free electrons.

One of us (D. B.) would like to express his sincerest thanks to Prof. M. N. Saha, F.R.S., whose keen interest made a prolonged stay at the Indian Institute of Science, Bangalore, possible.

Summary

It is shown that the original Dirac theory in which a particle of spin half $\hbar$ is described by the Dirac equation with all the negative energy states empty, and the hole theory in which all the negative energy states are filled each with one electron, do *not* in general lead to the same probabilities for second order processes, contrary to what is generally believed, due to the energy denominators in the quantum formula for a second order process being different in the two theories, although the matrix elements for each first order process are the same.

The formula for the scattering of radiation by a free electron on the hole theory is calculated. This is *not* the same as the Klein-Nishina formula which gives the scattering on the original Dirac theory. The new formula agrees with the Klein-Nishina formula only when the energy of the light quantum is small compared with the rest mass of the electron. For high energies it gives a greater scattered intensity at small angles and less at large angles than the Klein-Nishina formula and at extremely relativistic energies it gives a total scattering which is five times greater. The new formula at high energies is in definite disagreement with experiment, which agrees very well with the Klein-Nishina formula. Thus the hole theory is in definite

disagreement with experiments on scattering although it is in at least qualitative agreement with nature in describing the existence of the positron and the process of pair creation, and is the only form in which the Dirac theory is logically tenable.

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FLAVYLIUM SALTS CONTAINING PYRONE RINGS

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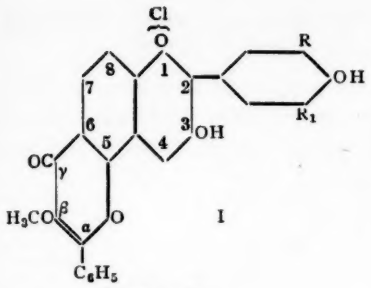
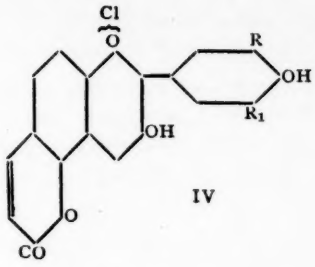
For establishing the presence of *o*-hydroxy-aldehyde groups, the pyrylium salt reaction is very handy. The formation of the bright red colour is useful for quick diagnosis and the solid pyrylium salts are convenient derivatives for analysis. In the course of other work in progress in these laboratories, information was needed regarding complex flavylium salts. As convenient examples, a number of them have now been prepared from 7-hydroxy-3-methoxy-flavone-8-aldehyde[1] and umbelliferone-8-aldehyde[2] by condensation with typical hydroxy acetophenones and their acetyl derivatives.

Besides the synthesis of flavylium salts of anthocyanidin type, Robinson and co-workers[3] made a number of synthetic flavylium compounds of simpler nature and studied them. They also made a few complex substances containing naphthalene and other condensed ring systems. Recently Russel and Speck[4] have reported the synthesis of a number of flavylium salts starting from β-naphthol-aldehyde. The formation of pyrylium salts of the xanthylium group by the condensation of 1 : 4-naphthohydroquinone and some aldehydes in the presence of hydrochloric acid has been observed by Fieser.[5] As a result of these investigations certain interesting observations regarding the influence of constitutional factors on fluorescence and colour reactions could be made and they may be useful for diagnosis of the constitution of unknown compounds.

With each of the two aldehydes, (1) 7-hydroxy-3-methoxy-flavone-8-aldehyde and (2) umbelliferone-8-aldehyde, the following three ketones have been condensed: (*a*) ω : *p*-dihydroxy-acetophenone,[6] (*b*) ω : 3 : 4-triacetoxy-acetophenone[7] and (*c*) ω : 3 : 4 : 5-tetra-acetoxy-acetophenone.[8] The reaction takes place quite readily and the flavylium salts are obtained in good yield. The two sets of compounds can be represented conveniently by the formulæ given below. The numbering of the positions is adopted with a view to emphasise the flavylium salt structure and the substituents in the pyrone ring are marked with Greek symbols treating the flavone derivatives as γ-pyrono compounds and the coumarin derivatives as α-pyrono compounds.



I



IV

I R=R$_1$=H
II R=OH; R$_1$=H
III R=R$_1$=OH

IV R=R$_1$=H
V R=O H, R$_1$=H
VI R=R$_1$=OH

The new flavylium salts exhibit no fluorescence in alcoholic or aqueous solutions. In sulphuric acid, however, the simplest members exhibit a green fluorescence, whereas the others give an almost negligible blue emission. Their solutions are comparatively feeble in colour in spite of the presence of pyrone rings. This may partly be due to the absence of hydroxyl group in the seven position. The α-pyrone derivatives give feebler colour reactions as compared with the γ-pyrone compounds. Not only are the chlorides sparingly soluble, but they are also very unstable. Recrystallisation should be effected from alcoholic hydrogen chloride. If aqueous alcoholic medium should be used for their crystallisation, the products contain very low percentage of halogen, probably due to partial conversion into the colour-bases. Even long exposure of the pure salts to atmosphere produces similar loss in halogen. Such products, however, give the same colour reactions as the original flavylium salts.

Experimental

The procedure for the preparation of the flavylium salts is given below using the simplest example and all the others are made similarly. Their properties and colour reactions are recorded in the form of Tables.

3:4′-*Dihydroxy*-5:6-γ-(α-*phenyl*-β-*methoxy*)-*pyronoflavylium chloride* (I).—7-Hydroxy-3-methoxy-flavone-8-aldehyde (0·4 g.) and ω: 4-dihydroxy-aceto phenone (0·2 g.) were dissolved in ethyl acetate (about 100 c.c.) and the solution was saturated with dry hydrogen chloride at 0° C. After the saturation, the current of gas was continued for about 2–3 hours and the flask with the contents was then left in the frigidaire overnight. The bright red crystalline solid was then collected and washed with ether (yield 83%). It was crystallised by dissolving in a small quantity of 5% methyl alcoholic hydrogen chloride and saturating it with dry hydrogen chloride gas in the cold. It

was obtained as bright red shining crystals which appeared as elongated rectangular plates under the microscope and melted at 227–29°.

In the case of the other ketones an anhydrous mixture of ethyl acetate and ethyl alcohol in equal proportions was employed as the solvent. During the course of the condensation, deacetylation took place giving rise to flavylium salts with hydroxyl groups.[8]

TABLE I

No.	Name of the Compound	Yield %	Appearance	Melting point	Analysis	
					Found	Calculated
	Flavylium salts obtained from 7-hydroxy-3-methoxy -flavone-8-aldehyde.					
I	3:4′-Dihydroxy-5:6-γ (α-phenyl-β-methoxy) pyrono-flavylium chloride $C_{25}H_{17}O_6Cl$, $2H_2O$	83	Red shining rectangular plates	227–29°	C, 61·7 H, 4·4 Cl, 7·6	C, 61·9 H, 4·3 Cl, 7·3%
II	3:3′:4′-Trihydroxy-5:6-γ (α-phenyl-β-methoxy) pyrono-flavylium chloride $C_{25}H_{17}O_7Cl$, $2H_2O$	60	Bright red micro-crystalline powder	240–42° (decomp.)	Cl, 6·5	Cl, 7·0%
III	3:3′:4′:5′-Tetrahydroxy-5:6-γ-(α-phenyl-β-methoxy)-pyrono-flavylium chloride $C_{25}H_{17}O_8Cl$, $4H_2O$	58	Dark red micro-crystalline powder	does not melt below 320°	Cl, 6·8	Cl, 6·4%
	Flavylium salts obtained from Umbelliferone-8-aldehyde					
IV	3:4′-Dihydroxy-5:6-α-pyrono-flavylium chloride $C_{18}H_{11}O_5Cl$, $\frac{1}{2}H_2O$	65	Deep brown micro-crystalline powder	255–57° (decomp.)	C, 61·1 H, 3·8	C, 61·4 H, 3·4%
V	3:3′:4′-Trihydroxy-5:6-α-pyrono-flavylium chloride $C_{18}H_{11}O_6Cl$, H_2O	65	Dark violet micro-crystalline powder	225–27° (decomp.)	Cl, 8·9	Cl, 9·4%
VI	3:3′:4′:5′-Tetrahydroxy-5:6-α-pyrono-flavylium chloride $C_{18}H_{11}O_7Cl$, $3H_2O$	91	Dark violet micro-crystalline powder	does not melt below 320°	Cl, 6·9	Cl, 6·6%

Colour reactions.—Solutions of the substances in 1% alcoholic hydrochloric acid were employed for all tests except 8 and 9 and the particular reagents were added. For the ferric chloride reaction an alcoholic solution without the acid was employed and for the study of fluorescence in concentrated sulphuric acid, the solids were directly used. All the compounds were

TABLE II

No.	Reagents	I	II	III	IV	B	VI
1	Colour of solution in 1% alcoholic HCl	Orange	Deep red	Deep red; violet tinge in thin layers	Orange yellow	Purple	Deep red
2	1% aqueous HCl ..	Very rapidly becomes colourless	Colour fades rapidly and becomes colourless	Turns pink and fades to very pale pink	Rapidly fades to colourless	Colour fades slowly to pale purple	Colour fades very slowly to pale red
3	20% HCl	Colour deepens; immediately precipitate forms	Colour deepens with a precipitate	Colour deepens and precipitate forms	Colour deepens; only slight precipitation	Colour not deepened	Colour not deepened
4	Sodium Acetate ..	Very pale yellow	Pale yellow	Turns pale yellow and then green	Immediately colourless	Pale blue	Light brown
5	Sodium Carbonate ..	First red, then quickly golden yellow	Yellowish brown	Brownish yellow changing to deep yellow	First pink and then yellow	Pale green	Brown
6	Sodium Hydroxide ..	Deep yellow	At first brown, rapidly fades to very weak yellow	Orange	Pale yellow to yellowish brown	Brownish yellow	Brown
7	Oxidation Test ..	Stable	Not very stable	Unstable	Stable	Not very stable	Unstable
8	Ferric Chloride ..	Not given	Olive green	Blue	Not given	Olive green	Blue
9	Conc. H_2SO_4 ..	Yellow solution with green fluorescence	Red solution with no fluorescence	Red solution with a violet tinge with very feeble blue fluorescence	Yellow solution with green-fluorescence	Red solution with negligible blue fluorescence	Pale violet solution with dull blue fluorescence

extractable by amyl alcohol and by the Cyanidin Reagent from aqueous solutions.

Summary

Flavylium salts containing γ- and α-pyrone rings have been prepared by condensing 7-hydroxy-3-methoxy-flavone-8-aldehyde and umbelliferone-8-aldehyde with hydroxy-aceto-phenones or their acetyl derivatives. They are found to have very feeble tinctorial properties and their fluorescence in concentrated sulphuric acid is not marked. The salts readily lose halogen and undergo conversion into colour bases.

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OCCURRENCE OF LUTEOLIN IN THE FLOWERS OF *CHRYSANTHEMUM INDICUM*

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(Communicated by Prof. T. R. Seshadri)

The pigments of the red, scarlet red and the deep red flowers of *Chrysanthemum indicum* L. were examined by Willstatter and Bolton,[1] and were shown to contain, besides carotene and xanthophyll, the anthocyanin chrysanthemin. The latter compound was also shown to be present in the flowers of *C. sinense*,[2] whilst apigenin was isolated in the form of its glucoside by Jacini from the petals of *C. leucanthemum*.[3]

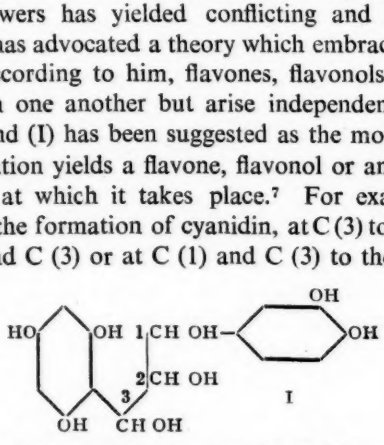
In continuation of our work on the anthoxanthins and their glycosides, the study of the yellow variety of the flowers of *C. indicum* has been undertaken, since there are certain points of interest in them. The flowers were obtained from Ambur in the North Arcot district during the month of November 1939. The colour of the petals was dull yellow and the size of the flowers varied from $1\frac{1}{2}$ to 2 inches in diameter. The petals contained a good amount of carotene, wax and resin which interfered with the separation of the anthoxanthins, and the interfering substances had to be eliminated at every stage during the course of the detailed examination carried out according to the general method described in some of our past publications.[4] On concentrating an alcoholic extract of the petals, carotinoid and some oily and waxy matter separated out. Subsequent dilution with water and extraction with petrol, chloroform and ether removed again the same type of substances. The aqueous solution on concentration yielded an anthoxanthin glucoside which underwent hydrolysis to produce glucose and a crystalline aglucone. The neutral lead acetate fraction was also found to contain a glucoside which gave the same products of hydrolysis. The basic lead acetate fraction was insignificant. Due to the small yields of the anthoxanthins and the presence of interfering impurities in considerable amounts, it was not possible to obtain the glucoside in a pure condition for purposes of identification.

The aglucone had the formula $C_{15}H_{10}O_6$, had all the characteristics of a tetrahydroxy flavone and did not melt below 300°. Its acetyl derivative was found to melt at 222–24°. Hence it was identified as luteolin, and the

identity was confirmed by taking the melting point of a mixture of the acetyl derivative with an authentic sample of tetraacetyl luteolin.

It is thus clear that the petals contain carotinoid material as the major component of the colouring matter, and luteolin is present only to a small extent in the form of its glucoside. The extracts of the flowers were examined for insecticidal properties, and were found to have no such value.

The occurrence of a glucoside of luteolin and chrysanthemin (cyanidin glucoside) in the yellow and the red varieties of *Chrysanthemum indicum* is noteworthy in regard to the biogenetic relationship between anthoxanthins and anthocyanins. The earlier view of Onslow[5] was that anthocyanidins were produced as the result of oxidation of the flavones, and the chief support was the existence of oxidising conditions in the plants having plenty of anthocyanins. When it was subsequently proved by Everest and Willstatter[5] that anthocyanidins were formed by the reduction of flavonols, the ideas had to be changed. In either case a correlation was expected between the constitutions of the anthocyanin and the anthoxanthin pigments. Examination of a number of flowers has yielded conflicting and inconclusive results. Recently Robinson[6] has advocated a theory which embraces all known experimental findings. According to him, flavones, flavonols and anthocyanidins are not formed from one another but arise independently from a common source, and compound (I) has been suggested as the most probable common intermediate. Oxidation yields a flavone, flavonol or anthocyanidin depending upon the point at which it takes place.[7] For example, oxidation at C (1) atom leads to the formation of cyanidin, at C (3) to the flavone luteolin, and at both C (2) and C (3) or at C (1) and C (3) to the flavonol quercetin.



I

Robinson and his collaborators[7] have concluded from a large amount of interesting data that cyanidin is the simplest of the anthocyanidins and is the first to be formed. The formation of others needs more steps in the synthesis. This explains why cyanidin is the most commonly occurring of the three fundamental anthocyanidins. A similar statement could be made regarding quercetin which is the most widely occurring of the flavonols. Though the results relating to the simultaneous occurrence of allied flavonols and anthocyanidins are not very many, still, wherever there is correlation, cyanidin and quercetin are concerned. This has been attributed by Robinson to their

abundant occurrence and might also be due to their fundamental nature in the evolution. In a similar way luteolin the most common of the naturally occurring flavones, and cyanidin should now be recognised as a related pair. More cases of this combination may be expected. In this connection it may be useful to analyse the red variety of the flowers of *C. indicum* for the anthoxanthins.

Experimental

Isolation of Luteolin.—The dried petals (6 kg.) of the flowers of *Chrysanthemum indicum* were extracted in batches with methylated spirit, and the combined extract was concentrated to about 800 c.c. The yellow waxy substances which separated during the course of the concentration was filtered through fluted filters, and the clear concentrate was allowed to stand. The waxy solid did not appreciably dissolve even in boiling alcohol, nor the solution did develop any prominent colour when treated with a drop of dilute alkali. It was evidently carotinoid in character and was, therefore, discarded. From the alcoholic concentrate no solid was deposited; but an yellow oil began to appear at the bottom of the flask. After six months, the mixture was diluted with a large volume of water, and extracted with petroleum ether which dissolved all the yellow viscous oil. Subsequent extraction with chloroform and ether removed some waxes and resins. The nature of the oil isolated is still under investigation. The aqueous solution was concentrated to a small bulk (500 c.c.) and set aside. After three months some brownish yellow solid (A) began to be deposited. It was filtered at the end of the third month and was found to contain a good amount of resin. The initial purification was effected by boiling it with water in which one part dissolved, while the other carotinoid part stuck to the sides of the test-tube. The clear solution on cooling deposited a pale yellow crystalline substance. Its further purification was not attempted for fear of losses. When boiled with 7% sulphuric acid, the compound underwent hydrolysis, and the aglucone separated out as a crisp yellow solid. After filtration of the products of hydrolysis, the filtrate was neutralised with barium carbonate, concentrated to a small bulk and treated with phenyl hydrazine in acetic acid solution. On heating the mixture for some time on a boiling water-bath, an osazone separated out, and it was identified as glucosazone from a study of its melting point and the crystal structure. The aglucone obtained crystallised from dilute alcohol as pale yellow needles, and the yield was 0·5 g. It did not melt below 300°. [Found: C, 59·3; H, 4·2; $C_{15}H_{10}O_6$, H_2O requires C, 59·2; H, 3·9%.] An alcoholic solution of the substance gave a brownish green colour with ferric chloride, a reddish orange

solution with a little dilute alkali and a yellow precipitate with lead acetate. With pH solutions the pigment did not produce any prominent colour changes. It dissolved merely to form yellow solutions. When boiled with acetic anhydride and anhydrous sodium acetate, it formed the tetraacetyl derivative which crystallised from dilute acetic acid as fine colourless needles and melted at 222–24°. [Found: C, 60·5; H, 4·5; $C_{15}H_6O_2(OCOCH_3)_4$ requires: C, 60·8; H, 4·0%.] All these properties indicated that the flavone was luteolin, and this was confirmed by taking the mixed melting point of the acetyl derivative with an authentic synthetic sample of acetyl luteolin.

Neutral Lead Acetate Fraction : Luteolin.—The mother-liquor left after the removal of solid (A) was treated with neutral lead acetate, when a yellow bulky precipitate was produced. After filtration the precipitate was suspended in water and decomposed in the usual way with hydrogen sulphide. The aqueous liquor produced thereby was concentrated and allowed to stand. Even after three months no solid came out. So the requisite amount of concentrated sulphuric acid was added so as to make the solution 7% in its acid content, and the mixture boiled under reflux. After half an hour a good amount of dark resin began to separate out and stick to the walls of the flask. The clear liquid was carefully decanted into another flask and the boiling continued when a brown resinous mass (solid B) came out after an hour. When the hydrolysis was over (two hours) the products were filtered while still hot. The clear filtrate did not yield any solid on cooling. It was, therefore, ether-extracted, when only a small amount of yellow crystalline substance was obtained. The acid solution was then neutralised with barium carbonate, and worked up for the isolation of the osazone as already described. The amount of the glucosazone formed was disproportionately high, when compared with the small amount of the pigment obtained by the ether-extraction of the filtrate from the products of the hydrolysis. Solid B should, therefore, have contained a considerable amount of the aglucone. It was brown in colour and highly resinous in character. After dissolving the substance in a small amount of pyridine, the solution was gradually diluted with water till the impurities began to separate as a suspension. They were then precipitated by the addition of calcium chloride and filtered off. The clear filtrate which did not develop any more turbidity on further dilution was concentrated and left overnight, when a yellow solid crystallised out. It was filtered and further purified by crystallisation from dilute alcohol, when it appeared as pale yellow needles not melting below 300°. It was also identified as luteolin, since the melting point of its acetyl derivative (222–24°) was not depressed by admixture with acetyl luteolin. The yield of the pure substance was 3 g.

The author's thanks are due to Prof. R. C. Shah for the supply of a synthetic sample of acetyl luteolin and to Prof. T. R. Seshadri for his interest in this work.

Summary

Luteolin is present in the form of its glucoside in the yellow variety of the flowers of *Chrysanthemum indicum*, whereas the red, scarlet red and the deep red variety contains the anthocyanin, chrysanthemin. Just as the simultaneous occurrence of quercetin and cyanidin is frequent, a similar correlation between the corresponding flavone, luteolin and cyanidin may also be common.

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ON NUMBERS OF THE FORM $2^a \cdot 3^b$ (I)

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§ 1. Let $N(x)$ denote the number of numbers of the form $2^a \cdot 3^b \leqslant x$, and $\Delta(x) = N(x) - F(x)$, where $F(x) = \frac{l(2x)\, l(3x)}{2\, l\, 2\, l\, 3}$, lx standing for $\log x$. Then Hardy, in his lectures on Ramanujan's work has proved that

$$\Delta(x) = 0\left(\frac{\log^2 x}{\log\log x}\right).$$

In this note I study $\Delta(x)$ from a different standpoint.

$[x]$ denotes the integral part of x and $\{x\} = x - [x]$.

A stands for a number of the form $2^a \cdot 3^b$. $\theta = \frac{l_2}{l_3}$.

§ 2. Theorem 1: *When* $x > y \geqslant 1$,

$$N(x) - N(y) = \left\{N\left(\frac{x}{2}\right) - N\left(\frac{y}{2}\right)\right\} + \left\{N\left(\frac{x}{3}\right) - N\left(\frac{y}{3}\right)\right\} - \left\{N\left(\frac{x}{6}\right) - N\left(\frac{y}{6}\right)\right\}.$$

Corresponding to every A $(y < A \leqslant x)$, which is a multiple of 6, there is one $A\left(=\frac{A}{2}\right)$ in $\left(\frac{y}{2}, \frac{x}{2}\right)$, one $A\left(=\frac{1}{3}A\right)$ in $\left(\frac{1}{3}y, \frac{1}{3}x\right)$, and one $A\left(=\frac{1}{6}A\right)$ in $\left(\frac{1}{6}y, \frac{1}{6}x\right)$. Corresponding to every A in (y, x), which is a multiple of 2 but not of 3, only $\left(\frac{1}{2}y, \frac{1}{2}x\right)$ will contain one $A\left(=\frac{A}{2}\right)$ but not the other intervals. A similar result is true for A which is divisible by 3 but not by 2. The converse results are also true. Since $x > y \geqslant 1$, if $y < A \leqslant x$, A should be either a multiple 2 or 3 or both. Hence the result follows immediately.

Theorem 2: $N(x) - N\left(\frac{1}{2}x\right) = \left[\frac{lx}{l3}\right] + 1$.

By putting $y = 1$ in theorem 1, we get

$$N(x) - N\left(\frac{x}{2}\right) = N\left(\frac{x}{3}\right) - N\left(\frac{x}{2\cdot 3}\right) + 1$$

$$N\left(\frac{x}{3}\right) - N\left(\frac{x}{2\cdot 3}\right) = N\left(\frac{x}{3^2}\right) - N\left(\frac{x}{2\cdot 3^2}\right) + 1$$

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. . . . . .

$$N\left(\frac{x}{3^r}\right) - N\left(\frac{x}{2\cdot 3^r}\right) = N\left(\frac{x}{3^{r+1}}\right) - N\left(\frac{x}{2\cdot 3^{r+1}}\right) + 1,$$

provided $\frac{x}{3^r} \geqslant 1$.

Choose r so that $\frac{x}{3^r} \geqslant 1 > \frac{x}{3^{r+1}}$, *i.e.*, $r = \left[\frac{lx}{l3}\right]$.

Then $N\left(\frac{x}{3^{r+1}}\right) = N\left(\frac{x}{2\cdot 3^{r+1}}\right) = 0$.

So adding the above we get the result.

THEOREM 3: $\Delta(x) - \Delta\left(\frac{x}{2}\right) = \frac{1}{2} - \left\{\frac{lx}{l3}\right\}$.

From theorem 2,

$$\frac{lx}{l3} - \left\{\frac{lx}{l3}\right\} + 1 = \left[\frac{lx}{l3}\right] + 1 = N(x) - N\left(\frac{1}{2}\,x\right)$$

$$= F(x) + \Delta(x) - F\left(\frac{1}{2}\,x\right) - \Delta\left(\frac{1}{2}\,x\right)$$

$$= \Delta(x) - \Delta\left(\frac{1}{2}\,x\right) + \frac{1}{2l2l3}\,[l(2x)\,l(3x) - lxl\left(\frac{3}{2}\,x\right)$$

$$= \Delta(x) - \Delta\left(\frac{1}{2}\,x\right) + \frac{1}{2} + \frac{lx}{l3}.$$

The result is immediate from this.

THEOREM 4: $\Delta(2^n) = \frac{1}{2}(n+1) - \sum_1^n \left\{r\frac{l2}{l3}\right\}$.

From theorem 3,

$$\Delta(2^n) - \Delta(2^{n-1}) = \frac{1}{2} - \left\{n\frac{l2}{l3}\right\}$$

$$\Delta(2^{n-1}) - \Delta(2^{n-2}) = \frac{1}{2} - \left\{(n-1)\frac{l2}{l3}\right\}$$

. . . . . .

. . . . . .

$$\Delta(2) - \Delta(1) = \frac{1}{2} - \left\{\frac{l2}{l3}\right\}$$

$$\Delta(1) = 1 - \frac{l2l3}{2l2l3} = \frac{1}{2}.$$

By adding we get the result.

THEOREM 5: $\Delta(2^a \cdot 3^b) = \Delta(2^a) + \Delta(3^b) - \frac{1}{2}$.

From theorem 3,

$$\Delta(2^a \cdot 3^b) - \Delta(2^{a-1} \cdot 3^b) = \frac{1}{2} - \left\{a\frac{l2}{l3} + b\right\} = \frac{1}{2} - \left\{a\frac{l2}{l3}\right\}.$$

. . . . . .

. . . . . .

$$\Delta(2 \cdot 3^b) - \Delta(3^b) = \frac{1}{2} - \left\{\frac{l2}{l3}\right\}.$$

Adding, $\Delta(2^a \cdot 3^b) - \Delta(3^b) = \frac{a}{2} - \sum_1^a \left\{r\frac{l2}{l3}\right\} = \Delta(2^a) - \frac{1}{2}$, from theorem 4.

THEOREM 6: $N(x) - N\left(\frac{1}{3}x\right) = \left[\frac{lx}{l2}\right] + 1$,

and $$\Delta(x) - \Delta\left(\frac{1}{3}x\right) = \frac{1}{2} - \left\{\frac{lx}{l2}\right\}.$$

The proof is similar to those for theorems 2 and 3.

THEOREM 7: If $s = [r\theta] = r\theta - \phi$, where $\theta = \frac{l2}{l3}$, then $N(2^r \cdot 3^s) = (r+1)(s+1) + rs$.

From theorem 3,

$$N(2^r \cdot 3^s) - N(2^{r-1} \cdot 3^s) = \left[\frac{r\,l2 + s\,l3}{l3}\right] + 1 = s + 1 + [r\theta].$$

$$N(2^{r-1} \cdot 3^s) - N(2^{r-2} \cdot 3^s) = s + 1 + [(r-1)\theta].$$

. . . . . .

. . . . . .

$$N(2 \cdot 3^s) - N(3^s) = s + 1 + [\theta].$$

By adding,

$$N(2^r \cdot 3^s) - N(3^s) = r(s+1) + \sum_1^r [\mu\theta]. \quad \text{From theorem 6,}$$

$$N(3^s) - N(3^{s-1}) = \left[\frac{s}{\theta}\right] + 1$$

. . . . . .

. . . . . .

$$N(3) - N(1) = \left[\frac{1}{\theta}\right] + 1.$$

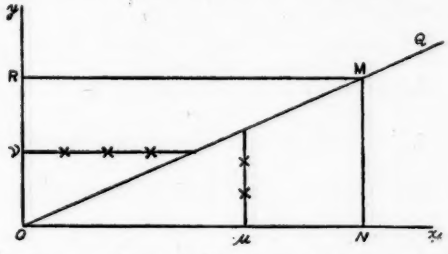
By adding

$$N(2^r \cdot 3^s) = r(s+1) + \sum_1^r [\mu\theta] + s + \sum_1^s \left[\frac{\nu}{\theta}\right] + N(1)$$

$$= (r+1)(s+1) + \sum_1^r [\mu\theta] + \sum_1^s \left[\frac{\nu}{\theta}\right]$$

$$= (r+1)(s+1) + S \text{ (say)}.$$

In the accompanying figure, OQ is the line $y = x\theta$; ON $= r$; M is the point of intersection of OQ and the line $x = r$; MR is drawn parallel to NO.



Now $[\mu\theta]$ = the number of lattice points on the line $x = \theta\mu$ between OM and ON, excluding the point $(\mu, 0)$. Hence $\sum_1^r [\mu\theta]$ = the number of lattice points in the triangle ONM excluding those on the x-axis.

Similarly we get that $\sum_1^s \left[\frac{\nu}{\theta}\right]$ = the number of lattice points in the triangle OMR excluding those on the y-axis. Since θ is irrational, (0, 0) is the only lattice point on OQ. Hence

S = the number of lattice points in the rectangle ONMR excluding those on the axes

$$= r\,[\mathrm{MN}] = r\,[r\theta] = rs.$$

Hence
$$\mathrm{N}(2^r \cdot 3^s) = (r+1)(s+1) + rs.$$

THEOREM 8: If $s = [r\theta]$ and $\phi = r\theta - s$, then

$$\Delta(2^r \cdot 3^s) = \frac{1}{2}(1-\phi)\left(1+\frac{\phi}{\theta}\right).$$

From theorem 7,

$$\Delta(2^r \cdot 3^s) = (r+1)(s+1) + rs - \frac{[(r+1)\,l2 + sl3)\,(rl2 + (s+1)\,l3)]}{2l2l3}$$

$$= \frac{1}{2}(r+1)(s+1) + \frac{1}{2}rs - \frac{1}{2}(r+1)\,r\theta - \frac{1}{2}s\,\frac{(s+1)}{\theta}$$

$$= \frac{1}{2}(r+1)(s+1) + \frac{1}{2}rs - \frac{1}{2}(r+1)(s+\phi) - \frac{1}{2}(s+1)\left(r - \frac{\phi}{\theta}\right).$$

$$= \frac{1}{2}\left(r+1-r\phi-\phi-r+\frac{s\phi}{\theta}+\frac{\phi}{\theta}\right)$$

$$= \frac{1}{2} - \frac{1}{2}r\phi - \frac{1}{2}\phi + \frac{1}{2}\phi\left(r - \frac{\phi}{\theta}\right) + \frac{1}{2}\frac{\phi}{\theta}$$

$$= \frac{1}{2}\left(1 - \phi + \frac{\phi}{\theta} - \frac{\phi^2}{\theta}\right) = \frac{1}{2}(1-\phi)\left(1+\frac{\phi}{\theta}\right).$$

THEOREM 9: If $r=\left[\frac{b}{\theta}\right]+1$ and $\phi=r\theta-b$, then

$$\Delta(2^a\cdot 3^b)=\Delta(2^a)-\Delta(2^r)+\frac{1}{2}(1-\phi)\left(1+\frac{\phi}{\theta}\right).$$

From theorem 5,

$$\Delta(2^a\cdot 3^b)=\Delta(2^a)+\Delta(3^b)-\frac{1}{2}$$

$$=\Delta(2^a)+\Delta(2^r\cdot 3^b)+\frac{1}{2}-\Delta(2^r)-\frac{1}{2}, \text{ from theorem 5.}$$

$$=\Delta(2^a)+\frac{1}{2}(1-\phi)\left(1+\frac{\phi}{\theta}\right)-\Delta(2^r), \text{ from theorem 8.}$$

Hence the theorem is proved.

Below I give a table of $A \leqslant 2^9$.

Table of numbers of the form $2^a\cdot 3^b$

	1		10		$2^{13}\cdot 3$		$2^{11}\cdot 3^4$
	2		2		$2^3\cdot 3^3$		3^{11}
	3		$2^7\cdot 3^2$		$2^{10}\cdot 3^3$		$2^8\cdot 3^6$
	2^2		$2^4\cdot 3^4$		$2^7\cdot 3^5$		$2^{16}\cdot 3$
	$2\cdot 3$		$2\cdot 3^6$		2^{15}		$2^5\cdot 3^8$
	2^3		$2^9\cdot 3$		$2^4\cdot 3^7$		$2^{13}\cdot 3^3$
	3^2		$2^6\cdot 3^3$		$2^{12}\cdot 3^2$		$2^2\cdot 3^{10}$
	$2^2\cdot 3$		$2^3\cdot 3^5$		$2\cdot 3^9$		$2^{10}\cdot 3^5$
	2^4		2^{11}		$2^9\cdot 3^4$		2^{18}
(10)	$2\cdot 3^2$	(50)	3^7	(90)	$2^6\cdot 3^6$	(120)	$2^7\cdot 3^7$
	$2^3\cdot 3$		$2^8\cdot 3^2$		$2^{14}\cdot 3$		$2^{15}\cdot 3^2$
	3^3		$2^5\cdot 3^4$		$2^3\cdot 3^8$		$2^4\cdot 3^9$
	2^5		$2^2\cdot 3^6$		$2^{11}\cdot 3^3$		$2^{12}\cdot 3^4$
	$2^2\cdot 3^2$		$2^{10}\cdot 3$		3^{10}		$2\cdot 3^{11}$
	$2^4\cdot 3$		$2^7\cdot 3^3$		$2^8\cdot 3^5$		$2^9\cdot 3^6$
	$2\cdot 3^3$		$2^4\cdot 3^5$		2^{16}		$2^{17}\cdot 3$
	2^6		2^{12}		$2^5\cdot 3^7$		$2^6\cdot 3^8$
	$2^3\cdot 3^2$		$2\cdot 3^7$		$2^{13}\cdot 2^2$		$2^{14}\cdot 3^3$
	3^4		$2^9\cdot 3^2$		$2^2\cdot 3^9$		$2^3\cdot 3^{10}$
(20)	$2^5\cdot 3$	(60)	$2^6\cdot 3^4$	(100)	$2^{10}\cdot 3^4$	(130)	$2^{11}\cdot 3^5$
	$2^2\cdot 3^3$		$2^3\cdot 3^6$		$2^7\cdot 3^6$		2^{19}
	2^7		$2^{11}\cdot 3$		$2^{16}\cdot 3$		3^{12}
	$2^4\cdot 3^2$		3^8		$2^4\cdot 3^8$		$2^8\cdot 3^7$
	$2\cdot 3^4$		$2^8\cdot 3^3$		$2^{12}\cdot 3^3$		$2^{18}\cdot 3^2$
	$2^6\cdot 3$		$2^5\cdot 3^5$		$2\cdot 3^{10}$		$2^5\cdot 3^9$
	$2^3\cdot 3^3$		2^{13}		$2^9\cdot 3^5$		$2^{13}\cdot 3^4$
	3^5		$2^2\cdot 3^7$		2^{17}		$2^2\cdot 3^{11}$
	2^8		$2^{10}\cdot 3^2$		$2^6\cdot 3^7$		$2^{10}\cdot 3^6$
	$2^5\cdot 3^2$		$2^7\cdot 3^4$		$2^{14}\cdot 3^2$		
(30)	$2^2\cdot 3^4$	(70)	$2^4\cdot 3^6$	(110)	$2^3\cdot 3^9$		
	$2^7\cdot 3$		$2^{12}\cdot 3$				
	$2^4\cdot 3^3$		$2\cdot 3^8$				
	$2\cdot 3^5$		$2^9\cdot 3^3$				
	2^9		$2^6\cdot 3^4$				
	$2^6\cdot 3^2$		2^{14}				
	$2^3\cdot 3^4$		$2^3\cdot 3^7$				
	3^6		$2^{11}\cdot 3^2$				
	$2^9\cdot 3$		3^9				
	$2^5\cdot 3^3$		$2^8\cdot 3^4$				
(40)	$2^2\cdot 3^5$	(80)	$2^5\cdot 3^6$				

ON NUMBERS OF THE FORM $2^a . 3^b$ (II)

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LET N (x) denote the number of numbers of the form

$2^a\, 3^b \leqslant x$, and $\Delta(x) = \mathrm{N}(x) - \log(2x) \log(3x)/2 \log 2 \log 3$.

Then from a result of Hardy and Littlewood, it follows that $\Delta(x)$ is not bounded, and as a matter of fact $\Delta(x) > c.\ \log\log x$ for infinitely many values of x. But from the table of the previous paper I, it was found that

$$|\Delta(x)| < 1 \text{ for all } x < 2^{19}.$$

This is rather surprising. So one of us prepared a Table of $s(n)$ for all $n \leqslant 1000$, where $s(n) = \sum_1^n f(r\theta)$, $f(x)$ being the fractional part of x and θ being $\dfrac{\log 2}{\log 3}$. From the previous paper

$$\Delta(2^n) = \frac{n+1}{2} - s(n).$$

By examining the Table for $s(n)$, it is found that

$$-0{\cdot}7822 < \Delta(2^n) < 1{\cdot}0731 \text{ for all } n \leqslant 1000.$$

Again from the previous paper

$$\Delta(2^a \cdot 3^b) = \Delta(2^a) - \Delta(2^r) + \mathrm{F},$$

where $\quad \mathrm{F} = \left(1 - \emptyset\right)\left(1 + \dfrac{\emptyset}{\theta}\right)/2$, $r = \left[\dfrac{b}{\theta}\right] + 1$, and $\emptyset = r\theta - b$.

Now $(1-x)\left(1+\dfrac{x}{\theta}\right)$ is maximum when $x = (1-\theta)/2$.

So

$$0 < (1-\emptyset)\left(1+\frac{\emptyset}{\theta}\right) \leqslant \left(1-\frac{1-\theta}{2}\right)\left(1-\frac{1-\theta}{2\theta}\right)$$

$$= \frac{1}{2}\left(1+\frac{\theta}{2}+\frac{1}{2\theta}\right) < 1{\cdot}06.$$

Hence when $x \leqslant 2^{1000}$.

$$\text{Min. } \Delta(2^a\, 3^b) \geqslant \text{Min. } \Delta(2^a) - \text{Max. } \Delta\, 2^r + \text{Min. F}$$

$$> -0{\cdot}7822 - 1{\cdot}0731 + 0 = -1{\cdot}8553.$$

$$\text{Max. } \Delta(2^a 3^b) \leqslant \text{Max. } \Delta(2^a) - \text{Min. } \Delta(2^r) + \text{Max. F}$$
$$\leqslant 1{\cdot}0731 - (-0{\cdot}7822) + 0{\cdot}53 = 2{\cdot}3853.$$

Hence we get the interesting result that when $x \leqslant 2^{1000}$

$$-1{\cdot}9 < \Delta(x) < 2{\cdot}4.$$

Though there are more than 300,000 numbers of the form $2^a 3^b$ up to 2^{1000}, yet Ramanujan's approximate formula does not differ from the actual result by more than 2·4. In view of the fact that $\Delta(x)$ is not bounded, the closeness of this approximation is remarkable. Further this forces one to wonder whether Ramanujan literally meant what he wrote to Hardy, namely, " the number of numbers of the form $2^u 3^v$ less than n is

$$\frac{\log(2n)\cdot\log(3n)}{2\log(2)\log 3}.$$

In conclusion, it may be noted that

$$\Delta(2^{558}\cdot 3^{173}) = \Delta(2^{558}) - \Delta(2^{275}) + \text{F}$$
$$> 1{\cdot}073 + 0{\cdot}782 + 0{\cdot}41 = 2{\cdot}265.$$

We give below a Table for $\Delta(2^n)$ in the range $(1 \leqslant n \leqslant 1000)$ for which $|\Delta(2^n)| > 0{\cdot}7$.

TABLE

n	$\Delta(2^n)+$	n	$\Delta(2^n)+$	n	$\Delta(2^n)-$
8	0·786531	531	0·703594	190	0·719406
10	0·798866	533	0·763463	191	0·726979
67	0·742143	539	0·800759	209	0·752266
73	0·858880	541	0·765753	210	0·747503
75	0·850355	550	0·877207	274	0·776447
411	0·706020	551	0·734943	275	0·782115
485	0·780206	552	0·961748	293	0·773109
487	0·885608	555	0·856587	294	0·766440
490	0·811738	558	1·073058	759	0·744074
493	1·5950	559	0·883356	760	0·750646
494	0·880229	560	1·062724	778	0·757921
495	1·070028	563	0·815250	779	0·752157
498	0·853845	566	0·889408	843	0·717056
501	0·959295	568	0·784199	844	0·721723
502	0·732586	642	0·717131		
503	0·874947	644	0·710607		
512	0·764358	972	0·725323		
514	0·799556	978	0·893789		
520	0·762838	979	0·713613		
522	0·703161	980	0·902507		
		986	0·786347		
		988	0·700190		

ESTIMATION OF CYSTINE BY NITROPRUSSIDE

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(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

A method for the quantitative estimation of cystine by the nitroprusside reaction was described by Blankenstein (1930). For reduction of the disulphide to cysteine potassium cyanide dissolved in boiling concentrated ammonia was used, a procedure which can be expected to cause appreciable destruction of the amino-acid. The values obtained by Blankenstein for the cystine content of the proteins analysed by him, notably in the case of serum globulin and albumin, were only a fraction of the amounts found to be present by other procedures and the method has not found general application. In view, however, of the known specificity of the nitroprusside reaction for thiol compounds under conditions such as prevail in protein hydrolysates in which the presence of carbonyl groups can be excluded and the various criticisms that have been made from time to time against the widely used Folin and Marenzi and Sullivan methods (Lugg, 1932 and 1933; Prunty, 1933; Shinohara, 1935), experiments were carried out to ascertain the conditions under which the reaction with nitroprusside could be utilised for the quantitative determination of cystine. The procedure found satisfactory is to reduce the cystine by means of sodium cyanide and sulphite as in the Sullivan method (Sullivan, 1937) and after addition of ammonia to allow the reaction with nitroprusside to take place in the presence of a small quantity of zinc sulphate which serves to stabilise the colour as shown by Shinohara and Kilpatrick (1934). Under these conditions colour production is proportional to the cystine present and cystine added to protein hydrolysates can be accounted for with an accuracy of 99%. The cystine contents of various proteins determined by this method are in good agreement with the values given by the Sullivan and Folin and Marenzi reactions.

Experimental

Reagents.—

1. Standard cystine solution containing 1 mg. of the amino-acid per 5 ml. of 0·2 N HCl.
2. 5% Aqueous sodium cyanide.

3. 20% Aqueous sodium sulphite.
4. 0·5 N Ammonium hydroxide.
5. 5% Aqueous sodium nitroprusside (to be prepared freshly before use).
6. 0·2 M Aqueous zinc sulphate.

Procedure.—To each 5 ml. of standard solution and the same volume of the test solution, also prepared in 0·2 N HCl, are added with shaking 2 ml. of NaCN followed by 1 ml. of Na_2SO_3. The solutions are mixed and let stand 1 minute. 10 ml. of ammonium hydroxide are added, followed after mixing and standing for 5 minutes, by 0·2 ml. of $ZnSO_4$. 1 ml. of nitroprusside is now added and after mixing the colours compared within 5 minutes.

The colour of the solution is magenta. At room temperature, 29° ± 2°, the colour maximum is reached instantaneously and remains stable for 6 to 7 minutes. If $ZnSO_4$ is omitted destruction of colour takes place rapidly, the intensity being reduced by about 10% in 3 minutes. Lowering of the temperature of the reaction increases the intensity of colour and advantage can be taken of this fact in dealing with very dilute solutions by working at ice temperature. 2 ml. of 0·1 M $HgCl_2$ or 6 ml. of 2 M H.CHO (Shinohara, 1936), added before the reagent, completely suppresses colour production. This can be used to detect the presence of colour-producing substances other than disulphide compounds.

Proportionality between colour intensity and cystine concentration.—The proportionality holds over a wide range and it can be seen from Table I that an unknown solution containing as much as six times the standard can be determined accurately.

TABLE I

Colour Intensity and Cystine Concentration

Standard mg.	Test soln. mg.	Reading of Std.	Reading of test	Cystine estimated (mg.)
1	0·5	20	39·7	0·503
1	1·5	20	13·3	1·50
1	2·0	20	10·0	2·0
1	3·0	20	6·8	2·95
1	4·0	20	5·1	3·92
1	5·0	20	4·1	4·89
1	6·0	20	3·4	5·88

Estimation of cystine in proteins.—0·2 to 0·3 g. of protein is hydrolysed with 20 parts of 20% HCl for 7 to 8 hours, the hydrolysate repeatedly

evaporated to dyrness *in vacuo* to remove as much of the acid as possible, taken up in water and neutralised to pH 3·5 with 10 N NaOH added drop by drop with constant stirring of the solution in order to prevent development of local alkalinity and consequent destruction of cystine. The solution is shaken up with 1 g. of kaolin and centrifuged, the residue washed with 0·1 N HCl, and the centrifugate and washings made up to a convenient volume, enough acid being added so that the aliquot taken for estimation contains about 0·8 to 1·5 mg. of cystine and 1 ml. of N HCl.

Recovery of added cystine.—Experiments conducted with different amounts of added cystine (from 0·5 to 1·5 mg.) resulted in quantitative recovery in all cases. The results of a typical experiment with 5 ml. of a serum globulin hydrolysate are tabulated below:

Hydrolysed serum globulin			Hydrolysed serum globulin +1·04 mg. of cystine			% Recovery of added cystine
Std.	Unknown	Cystine (mg.)	Std.	Unknown	Cystine (mg.)	
20	17·3	1·2	20	9·3	2·23	99

Cystine content of some proteins.—Determinations of cystine were carried out on the hydrolysates of proteins by the three methods, the Folin and Marenzi method as modified by Tompsett (1931), the Sullivan reaction and by means of nitroprusside; the results obtained together with those by previous authors are given in Table II.

TABLE II

% Cystine content of Proteins

(A, present analyses; B, other workers)

Protein	Folin and Marenzi (Tompsett)		Sullivan		Nitroprusside	
	A	B	A	B	A	B
Casein	0·33	0·30[1]	0·28	0·30[1]	0·29	
Edestin	1·44	1·36[2]	1·41	1·26[2]	1·46	
Gliadin	2·52	2·60[2]	2·39	2·60[2]	2·51	
Fibrin	2·02		1·84		2·18	1·3[3]
Serum globulin	2·41	2·25[1]	2·05	1·96[3]	2·53	0·80[3]
Egg albumin (B.D.H.) ..	2·69		2·15		2·59	
Anacardein	1·45		1·38		1·38	
Water melon globulin ..	1·19		1·19		1·19	

[1] Sullivan (1937); [2] Bailey (1937); [3] Blankenstein (1930)

Summary

The conditions for the use of the nitroprusside reaction for the quantitative determination of cystine are described. The method has the advantage of simplicity over the Sullivan reaction and is more specific than the Folin and Marenzi uric acid reagent.

My thanks are due to Prof. M. Damodaran for his interest in the work.

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